ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

FLUORINE CONTAINING COPOLYMERS

M. Sc. Thesis by

Leyla BAYKAL

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JUNE 2007

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FLOR İÇEREN KOPOLİMERLER

YÜKSEK LİSANS TEZİ

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ABBREVIATIONS

ATRP : Atom Transfer Radical Polymerization

FRP : Free Radical Polymerization

SFRP : Stable Free Radical Polymerization

CP : Controlled Polymerization

LP : Living Polymerization

C/LRP : Controlled/ “living” Polymerization

PDI : Polydispersity Index, (PDI=M_w/M_n)

scCO_2 : Supercritical Carbon Dioxide

TAN : Fluoroalkyl acrylate, $H_2C=CHCOOC_2H_4(C_2F_4)_nF$, n≈4

TM : Fluoroalkyl methacrylate , $H_2C=CCH_3COOC_2H_4(C_2F_4)_nF$, n≈3.5

***t*BA** : *tert*-butyl acrylate

P*t*BA : Poly(*tert*-butyl acrylate)

MMA : Methyl methacrylate

PMMA : Poly(methyl methacrylate)

PMDETA : N,N,N',N',N''-pentamethyldiethylenetriamine

EBrB : Ethyl 2-bromoisobutyrate

MBrP : Methyl 2-bromopropionate

BPO : Benzoyl peroxide

TFMA : 2,2,2-Trifluoroethyl methacrylate

HFMA : 1,1,1,3,3,3-Hexafluoroisopropyl methacrylate

PFDMA : 1H,1H,2H,2H-Perfluorodecyl methacrylate

THF : Tetrahydrofuran

DMF : Dimethylformamide

DMSO : Dimethylsulfoxide

TCE : Trichloroethylene

CCl_4 : Carbon tetrachloride

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FLUORINE CONTAINING COPOLYMERS

SUMMARY

Fluorinated polymers have attracted considerable recent interest, due to their chemical resistance, low surface free energy properties and oil/water repellence due to their hydrophobic properties.Amphiphilic fluorinated copolymers are of considerable interest for various applications. They may be utilized as emulsifiers, dispersion stabilizers, and compatibilizers. In particular, copolymers composed of fluorocarbon–hydrocarbon segments exhibit their own unique properties such as excellent chemical and thermal stability, low surface energy, and low refractive index and dielectric constant, which cannot be achieved by the corresponding non-fluorinated materials.

Several attempts have been reported to prepare fluorinated copolymers by means of cationic, anionic, living radical and group transfer polymerization, but few studies have addressed the synthesis of copolymers composed of a hydrophilic block and a fluorinated block. Their synthesis is limited by the need for high-purity monomers and solvents, reactive initiators and anhydrous conditions.

Atom transfer radical polymerization (ATRP) is a controlled free radical polymerization. This technique is one of the best route for the preparation of these well-defined amphiphilic block copolymers with controlled molecular weight, polydispersity, terminal functionalities, and chain architecture composition due to the relative ease of synthesis and their compatibility with a wide range of solvents.

In this study, fluorine containing vinyl copolymers were synthesized via free radical copolymerization method in solution and in supercritical carbon dioxide ($scCO_2$) and ATRP. For this purpose, monofunctional bromine end capped poly(*tert*-butyl acrylate), poly(methyl methacrylate), poly(2,2,2-trifluoroethyl methacrylate), poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate, poly(1H,1H,2H,2H-perfluorodecyl methacrylate) were synthesized and some of them having a definitive molecular weight used as macroinitiator for block copolymer synthesis via ATRP. On the other hand, copolymers which are composed of methyl methacylate and fluoroalkyl (meth)acrylates were also synthesized via free radical polymerization method in solution and in $scCO_2$ initiated by benzoil peroxide.

Then obtained copolymers were characterized using gel permeation chromatography (GPC) for molecular weight , ^{1}H-NMR and FT-IR spectroscopies for structure and contact angle measurements for surface properties.

FLOR İÇEREN KOPOLİMERLER

ÖZET

Flor içeren kopolimerlere olan artan ilginin sebebi, çok düşük yüzey enerjilerine sahip olmaları ve hidrofob özelliklerinden dolayı su/yağı üzerlerinde tutmamalarıdır. Amfifilik flor içeren kopolimerlerin de pek çok uygulama alanları vardır. Yüzey aktif maddesi, dispersiyon stabilizatörü ve uyumlaştırıcı (compatibilizers) olarak kullanılabilmektedirler. Özellikle, florokarbon-hidrokarbon parçalarından oluşan kopolimerler florlu malzeme içermeyen yapılarına kıyasla mükemmel kimyasal direnç, ısısal kararlılık, düşük yüzey enerjisi gösterirken, düşük refraktive indeks ve dielektrik sabitine de sahiptirler.

Flor içeren kopolimerleri hazırlamak için katyonik, anyonik, yaşayan radikal ve grup transfer polimerizasyonu gibi teknikler kullanılmakta olup çok az çalışma hidrofilik blok ile flor içeren hidrofobik bloktan oluşan kopolimer sentezine yöneliktir. Sentezleri yüksek saflıkta monomer, çözücü, reaktif başlatıcılar ve susuz koşullar gerektirdiğinden sınırlanmıştır. Atom Transfer Radikal Polimerizasyon (ATRP) kontrollü serbest radikal polimerizasyon yöntemidir. Bu yöntem iyi tanımlanmış, molekül ağırlığı kontrol edilebilen, düşük molekül ağırlığı dağılımına sahip, uç grup fonksiyonalitesi içeren ve farklı kompozisyonlarda zincir yapısından oluşan polimerleri ve özellikle amphiphilic blok kopolimerleri kolay sentez edebilmek için kullanılan ve bilinen çoğu çözücüler ile uyumlu en iyi yoldur.

Bu çalışmada, ATRP ile çözelti ve superkritik karbondioksit içinde serbest radikal kopolimerizasyon yöntemleri kullanılarak flor içeren vinil kopolimerler hazırlanmıştır. Bu amaçla tek fonksiyonlu brom uçlu; poli(*tert*-bütil akrilat), poli(metil metakrilat), poli(2,2,2-trifloroetil metakrilat), poli(1,1,1,3,3,3-hekzafloroisopropil metakrilat, poli(1H,1H,2H,2H-perflorodecyl metakrilat) sentezlendi ve kesin molekül ağırlığına sahip olanlar ATRP ile yapılan blok kopolimer reaksiyonlarında makrobaşlatıcılar olarak kullanıldı. Diğer yandan metil metakrilat ve floroalkil (met)akrilat içeren kopolimerler benzoil peroksit tarafından başlatılan serbest radikal polimerizasyonu yöntemi ile çözelti ve $scCO_2$ içinde polimerleştirilmişlerdir.

Daha sonra sentezlenen polimerler molekül ağırlığı için jel geçirgenlik kromatografisi, yapı için ^{1}H-NMR ve FT-IR spektroskopileri ve yüzey özellikleri için kontak açı ölçümleri kullanılarak karakterize edilmiştir.

1. INTRODUCTION

A block copolymer molecule contains two or more polymer chains attached at their ends. Linear block copolymers comprise two or more polymer chains in sequence, whereas a star block copolymers comprises more than two linear block copolymers attached at a common branch point. Polymers containing at least three homopolymers attached at a common branching point have been termed mixed arm block copolymers, although they can also be viewed as multigraft copolymers.[1]

Every year, new kinds of block copolymer are synthesized and their properties extensively studied. Due to their distinctive structures, block copolymers have useful and desirable properties. The addition of appropriate block copolymers into commodity plastics, such as polystyrene can enhance toughness, or modify the surface properties for applications as diverse as colloidal stabilization, medical implantation and microelectronic fabrication. Recent advances in theoretical investigations of the phase behavior of block copolymers materials enable the prediction of the morphology, domain size, interfacial widht and interfacial area of many types of block copolymers. These developments in applications and fundamental understanding of thermodynamics are driving forces to synthesize more interesting block copolymers. Advances in synthetic chemistry have created fresh opportunities for using judicious combinations of multiple blocks in novel molecular architecture to produce a seemingly unlimited number of exquisitely structured materials endowed with tailored mechanical, optical, electrical, ionic, barrier and other physical properties. Block copolymers are prepared by joining two or more distinct polymer blocks together. The constituent polymers are often thermodynamically incompatible. The block coplymers can be divided into two categories from the point of view of topology: linear and nonlinear. A linear AB diblock copolymer consists of a chain of monomers of type A attached at the end of to a chain of type B monomers. Similarly, the chains of monomers A, B and C or more monomer types are joined together to form ABC triblock copolymer or multiblock copolymers. When three or more different polymer chains are connected

at one point, one of the types of nonlinear block copolymers, a miktoarm star copolymer is formed. In most polymer synthesis, normal chemical kinetics results in a distribution of molecular weights, and in block copolymers, this will produce compositional heterogeneity. This can be avoided by adopting so-called 'living' polymerization techniques. [2]

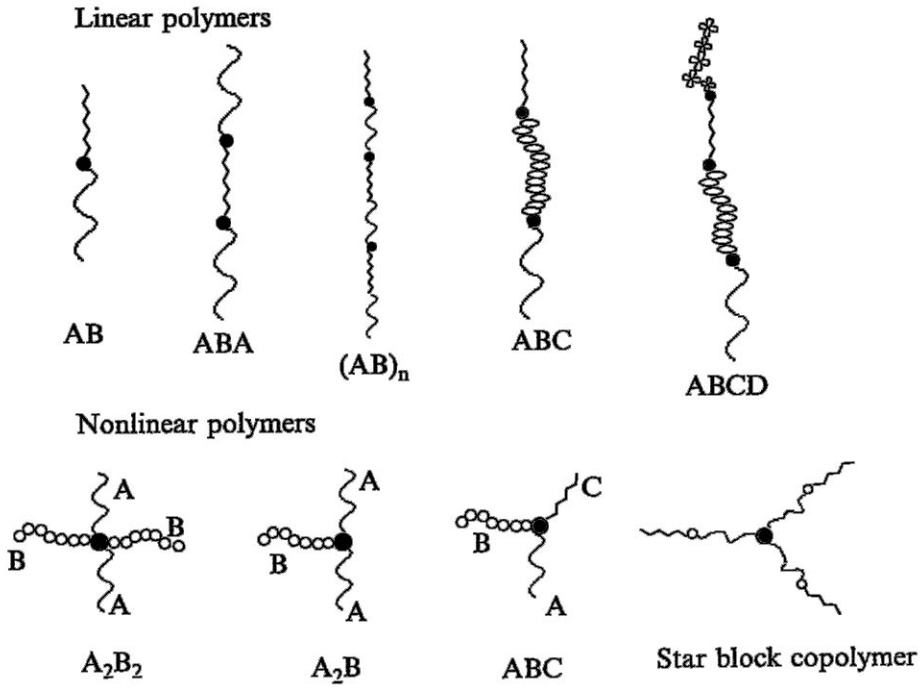


Figure 1.1: Block Copolymers

Fluorinated polymers have always attracted significant attention due to high thermal stability, good chemical resistance, excellent mechanical properties at extreme temperatures, superior weatherability, oil and water repellence and low flammability in addition to low refractive index.[3] Several attempts have been reported to prepare semi-fluorinated copolymers by means of cationic, anionic, living radical, and group transfer polymerisation, but these techniques have been limited by the need for high-purity monomers and solvents, reactive initiators and anhydrous conditions.[4] The development of fluoropolymers began with the invention of polytetrafluoroethylene (PTFE) in 1938 by Dr. Roy Plunkett of DuPont Company, continuing in 1992 when a soluble perfluoropolymer (Teflon AF) was invented, while fluoroplastics polymerized in supercritical carbon dioxide($scCO_2$) were introduced in 2002. Besides these commercially important examples many other routes toward fluorinated materials have been researched intensively by both academic and industrial teams. These efforts have led to the emergence of various

functional materials with notable properties: biomaterials, surfactants, lubricants, insulators, ion conducting materials (e.g. for Li-ion batteries) and proton conducting materials (e.g. for membranes for fuel cells). A number of materials such as paints and coatings as well as materials for the optic and electronic industries have additionally been developed.

The outstanding contribution in the past decade of the controlled radical polymerization (CRP) methods [5] allowed for development of advanced well-defined copolymers with various architectures (block, star, dendritic, alternating or graft) having predictable molecular weights and low molecular weight distributions. These techniques also permit advanced fluorinated materials to be synthesized. Extensive research engaging the three main controlled radical polymerisation techniques, namely atom transfer radical polymerisation (ATRP), nitroxide-mediated radical polymerization (NMP) and reversible addition–fragmentation chain-transfer (RAFT), have furnished various fluorinated materials and architectures, where ATRP has been the dominating technique for the synthesis of well-defined copolymers with controlled molecular weight, polydispersities, terminal functionalities, and chain architecture composition. [6]

Synthesis of well-defined fluorinated copolymers using the three above-mentioned techniques, and being involved in ATRP of fluoromonomers. Fluoromonomers can be polymerized by CRP methods in bulk or in solution in common solvents, which are often involved for the copolymerisation with non-fluorinated monomers.
Specific fluorinated solvents, ionic liquids and $scCO_2$ have also been employed as reaction media. Sometimes also another part of the catalytic system (e.g. ligands in ATRP) is preferred to be fluorinated. [7]

CRP methods generally rely on a reversible activation-deactivation process between dormant and active polymer chains, and as the double bond of monomers containing fluorine is additionally activated by the electron withdrawing group, this sometimes leads to considerably higher rates of polymerisation compared to the non-fluorinated analogues. This in turn allows for the possibility of using either the macroinitiator method or the sequential monomer addition method for the synthesis of F-containing copolymers.

The definition of living polymerization is a polymerization reaction, where no unwanted side reactions such as transfer or termination take place, and where all polymer chains are initiated simultaneously. This means that the growing ends of the polymer chains are active indefinitely and that an ideally living system should yield polymers with polydispersities of 1.0. In reality no such reactions have been found, but some systems are not far from achieving this goal. For these reaction systems a number of terms have been used including ‘‘living’’, pseudo-living, quasi-living and living/controlled, which has led to confusion and frustration among researchers in the field. [8] It is prefered the term controlled polymerization, which will be used to describe reactions that fulfil the following criteria:

- Kinetics are first order with respect to the monomer.
- Degree of polymerization is directly proportional to the initial monomer to initiator ratio.
- Narrow molecular weight distributions are obtained.
- After consumption of monomer the reaction can continue by addition of new monomer.

In free radical polymerization the active polymer chains can react with one another either by radical combination or by disproportionation, which can lead to broad molecular weight distributions, furthermore chain transfer often plays a disturbing role. For some applications a narrow molecular weight distribution in the polymer is necessary, which has led to the development of a number of techniques whereby control of the polymerization reaction is obtained, termed controlled radical polymerization reactions.

The strategy for eliminating undesirable termination reactions has been to ensure that only a fraction of the polymer in question is activated at a time, i.e. present as an active radical, while the majority of polymer chains are in a dormant/inactivated state. A dynamic equilibrium between the two states must exist in order for the growth of the polymer chains to be equal. [9]

In order to study the properties of fluorinated (meth)acrylate, homopolymers and blockcopolymers were designed and synthesized by ATRP and also many copolymers were synthesized by FRP in solution and in $scCO_2$. For this purpose, *tert*-butyl acrylate(*t*BA), Methyl methacrylate(MMA), 1H,1H,2H,2H-perfluorodecyl methacrylate(PFDMA), 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFMA),2,2,2-trifluoroethyl methacrylate (TFMA) were synthesized as a homopolymer and some of them were used as macroinitiators for block copolymerization via ATRP.

Second, Methyl methacrylate with ZONYL TAN® or ZONYL TM® by DUPONT, acrylate and methacrylate derivatives respectively, were copolymerized via FRP both in solution and in $scCO_2$ to compare surface properties of fluorine contains with other fluorinated monomers.

2. THEORETICAL PART

2.1 Fluorinated Polymers

The fluorine atom is well known to be effective in which to produce the low free energy surface, because the fluorine atom possesses a small atomic radius and the biggest electron negativity, so it forms a stable covalent bond with the carbon atom.[10]

Fluorinated polymers are classified in a rather unique group of polymer materials. The fluorination modifies the physicochemical properties of the original polymers and induces the novel properties of polymers. Especially, fluorinated block copolymers possess the characteristic properties of both fluoropolymers and hybrid polymers. [15] Block copolymers with perfluoroalkyl side chains are known to be an amphiphilic surfactant and form the micelles in many solutions such as aqueous and organic solvents, due to the poor solubility of the perfluoroalkyl side chains.[10]

Fluorinated polymers are well known as low surface energy materials, which have oil- and water repellent surface and have been proposed for coating of substrates such as textiles, papers, leather, wood,etc. When the surface is uniformly covered with a trifluoromethyl (CF_3) array, a very low surface energy surface can be achieved. The surface activity of fluorine-containing block copolymers is intensely dependent on the effective and efficient use of fluorine. The former refers to the amount that the addition of fluorine lowers the surface tension relative to the parent material, and the latter refers to the minimum concentration of fluorine necessary to reach the minimum surface tension. [19] The surface component, orientation packing and end groups will affect the surface behaviour of the polymer films.[21] There are many methods used for incorporation of fluorine [16] content into polymer, such as plasma treatment, grafting reaction and living polymerization. The structure of polymer influences its surface-active property, so controlling the distribution of fluorine atoms within polymer is very important. Living anionic, living cationic, group transfer polymerization and the method of iniferter [22] polymerization have

been used to prepare well-defined fluorinated polymers. But these have their own disadvantages, such as rigorous reaction conditions or limited monomers and so on. Fluorinated surfaces derive their characteristics from the unique molecular properties associated with the C–F bond that impacts a specific chemistry and physics at interfaces. Their low surface tensions, low electrostatic loading and low friction coefficient can play an essential role in microelectronics, antifogging and antifouling applications and are promising in medical field. Physicochemical and structural studies of acrylate/methacrylate polymers with perfluoroalkyl side chains have been reported in literature and have shown a direct relationship between the organization of the fluorinated side chains and the surface properties of the coatings prepared with the various polymers.[17] Copolymerization of fluorinated monomers with hydrocarbon homologous could be one of the solutions to avoid the poor solubility of fluoropolyacrylates homopolymers in current organic solvents. By systematically probing the effect of structure on the surface properties of the corresponding films, study of these polymers has helped optimize the semifluorinated side groups for creating low surface energy materials. [14]

Most investigations of amphiphilic copolymers [18] have been for systems containing one hydrophobic block such as styrene, acrylamide, and cinnamoylethyl methacrylate and one hydrophilic block like acrylic acid, vinylpyridine, cesium acrylate, and ethylene oxide. In other cases, both blocks in the copolymers are hydrophobic or hydrophilic, but the tendency is different between blocks. Many investigations use transmission electron microscopy (TEM), atomic-force microscopy (AFM), light scattering, fluorescence spectroscopy, small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), potentiometric titration, microcalorimetry, and electrokinetic analyzer to characterize the copolymers. The copolymers may form micelles of reverse molecular arrangements in aqueous and nonaqueous media as well as surfactant micelles. [11]

Fluorinated polymers are highly solvophobic. For improving the solubility of fluorinated polymers in solvents, hybrid compounds with non-fluorinated moieties are synthesized. Then, amphiphilic copolymers are soluble and self-associated in solvents. Incorporation of fluorinated moieties in polymers is carried out using

different methods: (1) participation of fluorinated unit in main chain; (2) modification of polymer terminals by fluorinated derivatives; and (3) fluorination of polymer side chains.

2.1.1 Fluorinated Homopolymers

In linear polymers, fluorine atoms were included in main chain, terminal and side chain.

Main-chain fluorinated polymers, poly(ether urethane)s and poly(ether urethane urea)s including various perfluoro chain extenders (Fig.2.1a), are synthesized.[52-55] The segmented fluorine distribution on the surface and in the bulk of solvent-cast films depend on annealing, casting solvent and casting condition. The miscible blend of fluorinated polymers, poly(vinylidene fluoride), with poly(1,4-buthylene adipate) are investigated as functions of blend composition and temperature. At temperatures between melting points of two polymers, the amorphous poly(1,4-buthylene adipate) has been incorporated between the crystalline poly(vinylidene fluoride) lamellae in the blends containing up to 50 wt.% of poly(1,4-buthylene adipate). At temperatures below a melting point of poly(1,4-buthylene adipate), the poly(vinylidene fluoride) and poly(1,4-buthylene adipate) lamellae were in the segregated arrangement. These investigations provided the insight into the lamellar organization of the blends between fluorinated and non-fluorinated polymers.

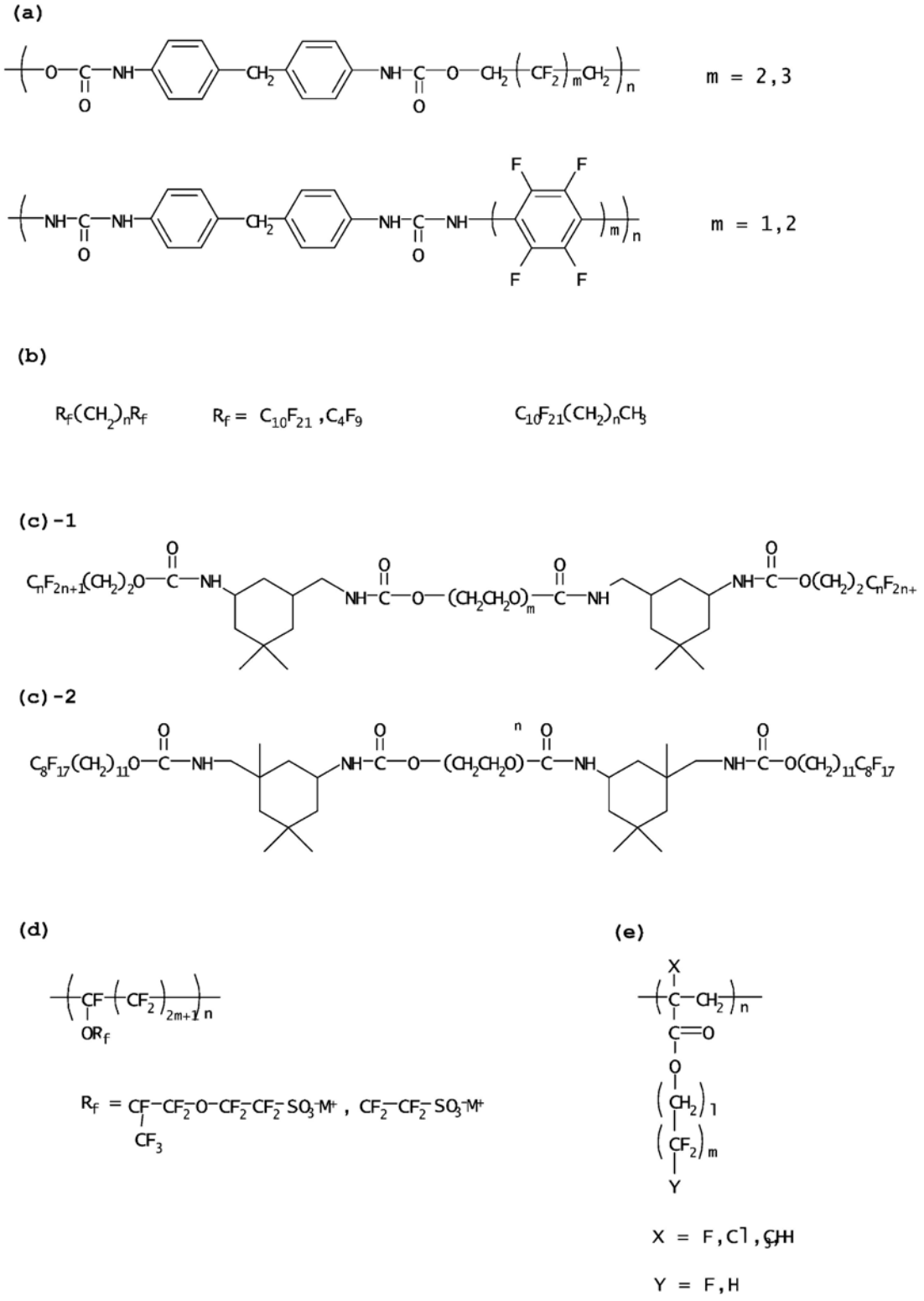


Figure 2.1: Fluorinated Homopolymers

End-cap fluorinated polymers, linear polyethylenes with fluoroalkyl end groups (Fig.2.1b), have been prepared by ring-opening metathesis polymerization of cyclododecane in the presence of partially fluorinated acyclic olefins, followed by

reduction of the double bonds in the backbone. [55]

The polyethylenes with two perfluorinated ends were the most effective for lowering melt surface tension. Very high advancing contact angles in hexadecane indicate a high surface concentration of perfluorinated species with close-packed CF_3 groups.

The surface properties of blends of a lower molecular weight end-cap fluorinated polyethylene with a polyethylene were compared with a series of pure end-cap fluorinated polyethylene. At similar bulk fluorine levels in the blends and pure polymer, the surface fluorocarbon content in the blends was significantly enhanced.

Polyethylene oxides end-capped with short fluorocarbon chains (Fig. 2.1c-1) have been synthesized and characterized.[56] In an aqueous solution, the fluorocarbon portions associated strongly to form micelle-like structures, which are bridged by polyethylene oxide chains to forma three-dimensional network. As a result, these polymers in the solution exhibited unusual rheological properties as a function of fluorocarbon length and polymer concentration. The viscosity was dramatically enhanced by replacing the end-cap C_6 F_{13} with C_8 F_{17} as a consequence of the stronger association interaction of C_8 F_{17} in aqueous solution. Between 2 and 6 wt.% concentrations, both systems were characterized by a similar concentration of chains bridging micelles in each system.

If the influence of the end-cap on the linear viscoelasticity of aqueous solutions of end-cap perfluorinated poly(ethylene oxide) (Fig. 2.1c-2) has been investigated as a function of the polymer concentration, polymer chain length, degree of functionalization, additive surfactant and temperature , the steep increase of the static viscosity attributed to the sol–viscoelastic transition observed with the formation of the multiconnected network. It is denoted in the present work that the hydrophobic character of the end caps reinforced by the perfluorinated segments leads to larger relaxation times and higher activation energies as compared with those of hydrocarbon-type polymers.

Polymers composed of a poly(tetrafluoroethylene) backbone with perfluoro pendant side chains terminated by an ionic group (Fig. 2.1d) are called perfluorinated ionomers. [57] The colloidal structure of short pendant chain perfluorinated ionomer in polar solvents has been compared with that of long pendant chain analog. Both ionomers formed rod-like shape aggregates. The significantly smaller cross-sectional aggregate radius (1.5–1.7nm) for short pendant chain ionomer, in comparison with

that (2.0–2.5 nm) for long pendant chain ionomer, in aqueous solutions is attributed to the smaller molecular weight.

Side chain-fluorinated polymers, poly(fluoroalkyl substituted acrylate)s (Fig.2.1e) were synthesized and dielectric measurements were carried out on them over a wide temperature range at different frequencies.[58] In polymers with X=F, there were three relaxations at above 400 ^{o}K, approximately 250 ^{o}K and below 150 ^{o}K. Those were attributed to a reorientational motion of long segments at above glass-transition temperature, a rotational motion of carbonyl groups in amorphous region and an internal motion of fluoroalkyl side chains, respectively. As the fluoroalkyl chain length increases, the internal motion relaxation sifted to higher temperatures in a polymer with Y=F but it was almost uncharged in a polymer with Y=H, while the reorientational motion relaxation moved to higher temperatures in both polymers. This report demonstrates that the dielectric relaxation behavior is highly attributed by the chemical structures and the existence of crystallites, that is, the ordering of main backbone chains and fluoroalkyl side chains.

2.1.2 Fluorinated Diblock Copolymers

In order to increase their solubility in solvents, solvophilic nonfluorinated polymer block is bound to fluorinated polymer block. Such block copolymers sometimes behave as amphiphilic polymers.

Copolymers of acrylamide and 2-(N-ethylperfluorooctanesulfonamido)ethyl acrylate have been synthesized and their aggregation behavior was investigated in water. The copolymers displayed the critical aggregation concentration depending on the amount of fluorinated block and the polymer concentration. Derivatives of poly(sodiumacrylate) bearing a few mole percent of perfluoroalkyl side chains (Fig. 2.2a) also displayed an associating behavior, as indicated by very high viscosity.[59] Mixing of the perfluorinated copolymers with their hydrogenated analogues or with hydrogenated surfactants is not ideal for low modification ratios of perfluorination and at concentration ranges close to the critical aggregation concentration of polymers.

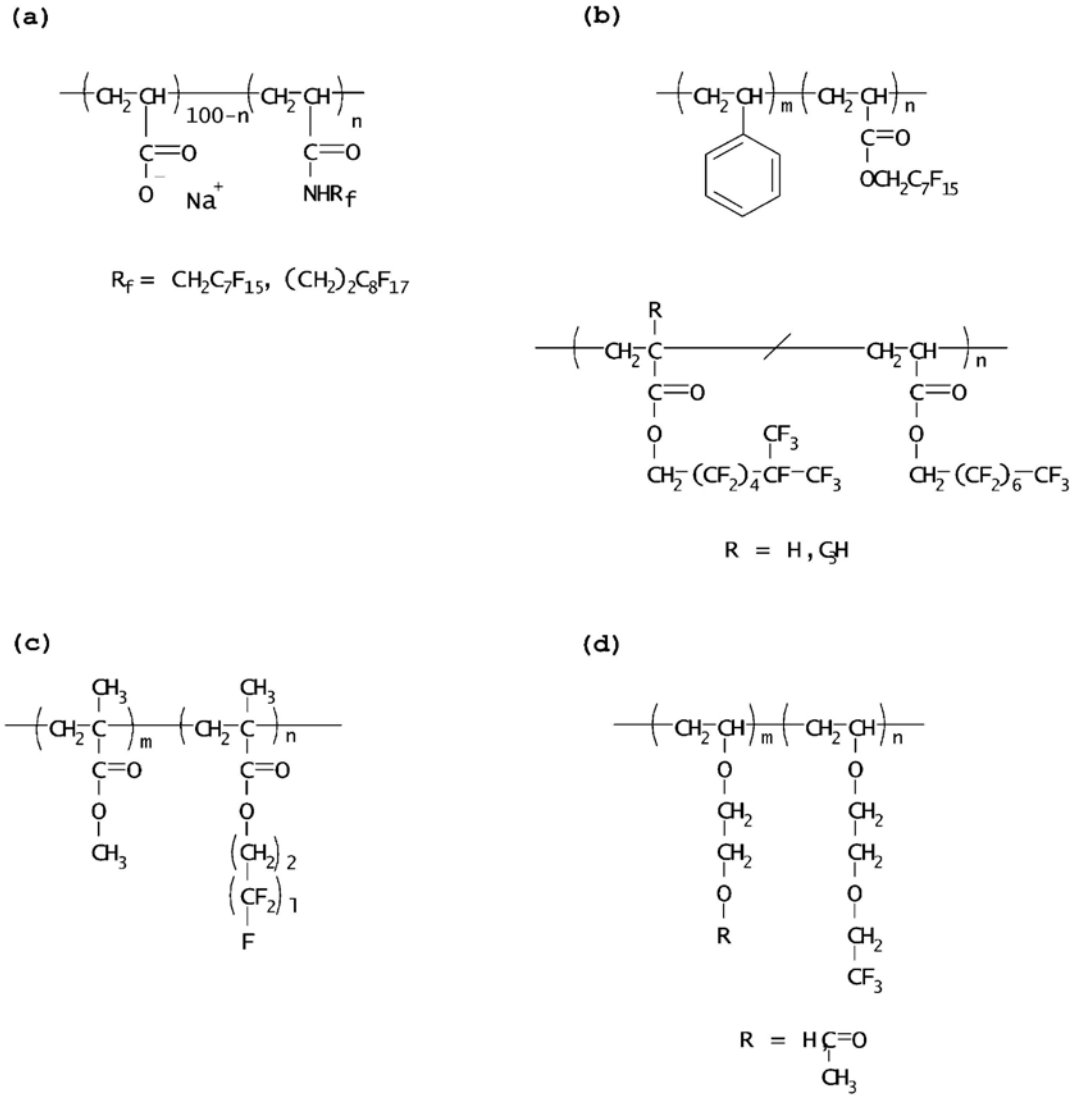
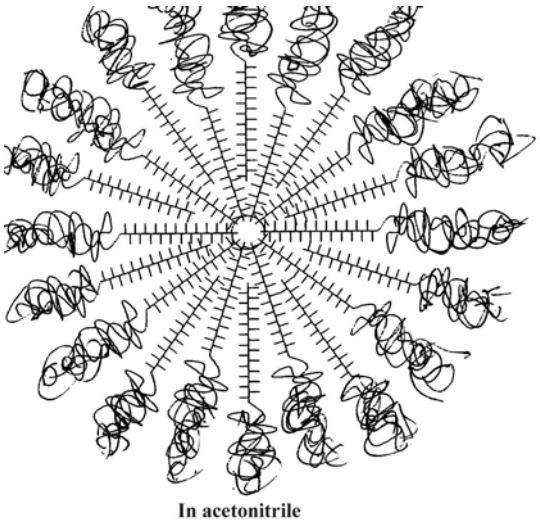


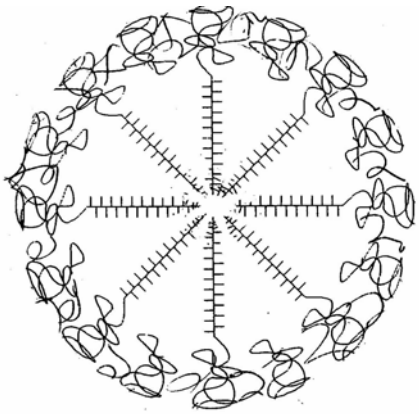
Figure 2.2: Fluorinated Diblock Copolymers

The surface characteristics of diblock copolymers consisting of both a fluorocarbon block of poly(1,1-dihydroperfluorooctyl acrylate) and a hydrocarbon block of polystyrene (Fig. 2.2b) as well as various novel fluorinated acrylate homopolymers has been investigated. Fluorine and the fluorine-containing constituents were surface enriched relative to carbon and oxygen from the acrylate portions of the homopolymers. This effect also occurred in the diblock copolymers, where the 1,1-dihydroperfluorooctyl acrylate block preferred the polymer–air interface.

Semifluorinated diblock copolymers based on methyl methacrylate and 1H,1H,2H,2H-perfluoroalkyl methacrylates (Fig.2.2c) were prepared by nucleophilic-catalyzed group transfer polymerization.[60] The surface activity of the materials and the formation of micelles were revealed in toluene. While the block copolymer formed cylindrical micelles, the coexistence of the poly(methyl methacrylate) homopolymer shifted the association equilibrium to the side of spherical aggregates. Micelles were formed with the fluorinated blocks turned inside the core and the non-fluorinated blocks located at the corona. However, the surface of thin polymer films cast from a toluene solution consisted mainly of the fluorinated block. During the film formation, monomeric polymers covered the surface with fluorinated block at the airside. Association of poly(methyl methacrylate)-*block*-poly(2-perfluorooctylethyl methacrylate) copolymers has been examined in organic solvents. Block copolymers were self-assembled into larger aggregates in acetonitrile than in chloroform, since the former is a poor solvent in comparison with the latter. [11,18]



In acetonitrile



In chloroform

Figure 2.3: Polymer Micelles in Acetonitrile and in Chloroform

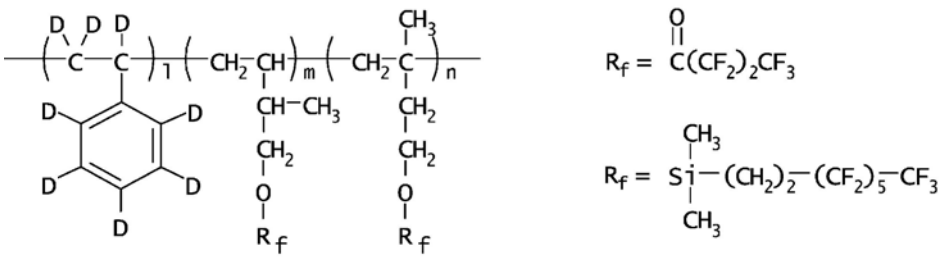
Spherical particles in microscopic morphologies consisted of a core of fluorinated block and a shell (corona) of nonfluorinated block. The particles in acetonitrile were typical polymer micelles of approximately 15-nm core radius and approximately 15-nm corona thickness, while those in chloroform were 'crew-cut' aggregates. The solvent penetration into polymer micelles in acetonitrile is less in the core than in the shell. Two types of amphiphilic block copolymers, poly(2-hydroxyethyl vinyl ether)-block-poly(2-(2,2,2-trifluoroethoxy)ethyl vinyl ether) (Fig. 2.2d) and poly-(2-hydroxyethyl vinyl ether)-block-poly(n-butyl vinylether) were synthesized, having the same ratios of polymerization degree in hydrophilic and hydrophobic segments with the same total chain length. The micelle formation and the solubilization of various fluorinated and non-fluorinated compounds were examined in aqueous solutions of these polymers. The hydration of filmsurfaces consisting of poly(amide urethane) block copolymer with fluorinated side chains (Fig. 2.2e) has been studied. A film, which was initially prepared in air and annealed above the glass transition temperature, underwent significant surface morphology change upon immersion in aqueous solution. The pH dependence of the adhesion force varied with surface morphology. Both hydrophobic and hydrophilic blocks were partially hydrated within minutes and underwent further hydration on longer time scales up to days.

2.1.3 Fluorinated Multiblock Copolymers

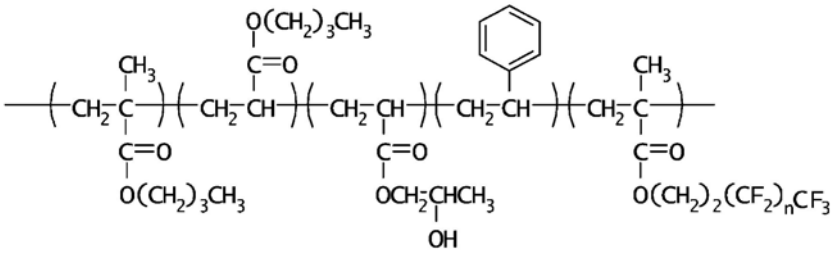
A diblock copolymer of deuterated styrene and isoprene with a small volume fraction of isoprene is chemically modified to incorporate pendant-fluorinated functional side chains (Fig. 2.4a) Acrylic polymers containing fluorinated units (Fig.2.4b) have been prepared by free radical solution polymerization of a variety of hydrocarbon monomers with the (perfluoroalkyl)ethyl methacrylate monomer. Polymers were prepared using two different methods of feeding monomer into the reaction mass. The resultant (perfluoroalkyl)ethyl methacrylate-containing acrylic polymers were quite surface active in the solid state, although the magnitude of surface activity depended on the monomer feed method. The concentration profile of fluorine in the films exhibited a steep gradient normal to the surface. This investigation demonstrates that a variety of surfaces could be constructed by incorporating

fluorinated isocyanate with the various acrylic copolymers.

(a)



(b)



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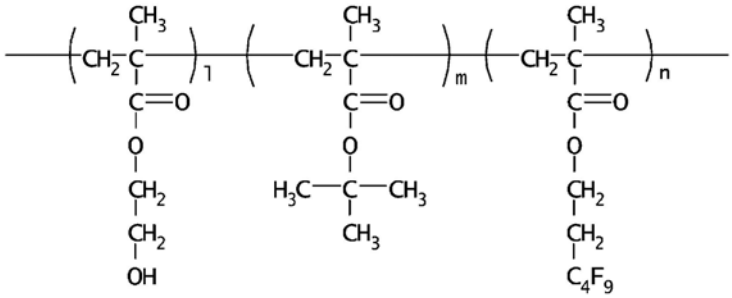


(d)

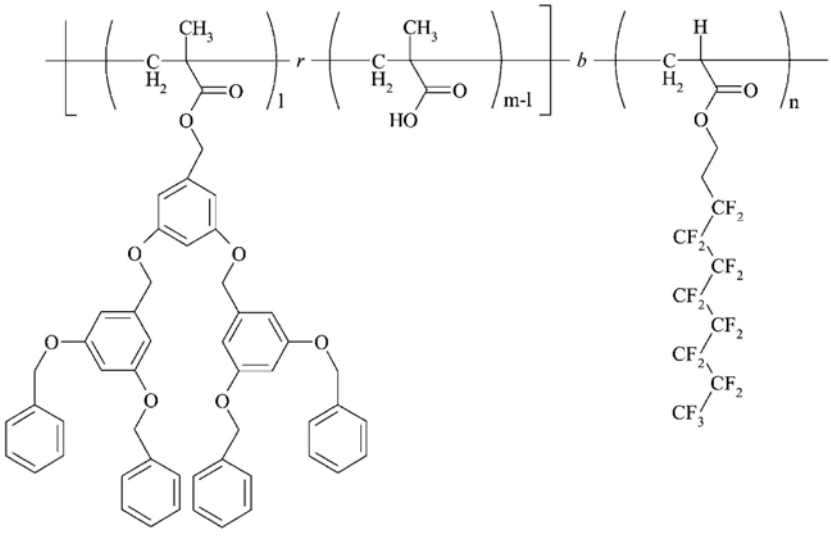


Figure 2.4: Fluorinated Multiblock Copolymers

Three homopolymers of perfluoroalkyl methacrylates, 2,2,2-trifluoroethyl-, 2-(perfluorobutyl)ethyl- and 2-(perfluorooctyl)ethyl-methacrylates and ABC triblock copolymers of methacrylates containing hydrophilic, hydrophobic and perfluoroalkyl groups (Fig. 2.4c) have been synthesized. Triblock copolymer enriched the poly(2-(perfluorobutyl)ethyl) segment at the dry film surface. Three-phase lamellar microdomain structure was observed in ABC triblock copolymer films and the four-layer lamellae model successfully reproduced the observed profile. This report confirms the surface rearrangement accompanying the change of the environmental conditions. Recently, di- and triblock copolymers of tert-butyl methacrylate and 2-(N-methylperfluorobutanesulfonamido) ethyl methacrylate have been synthesized. The microphase separation was observed in the cast film. When tert-butyl methacrylate block was converted into anhydride and then into the sodium salt of methacrylic acid, the resultant block copolymers were soluble in water, if the content of fluorinated block was less than 10 mol.%. For these block copolymers, the aggregation behavior was dominant even at very low concentrations.

2.2 Applications of Fluorinated Polymers

Novel fluorinated polymers have various commercial uses as coating materials, forming agents, lubricants, and so on, because they exhibit extremely low surface energies. Thomas et al. have reported surface properties of acrylic polymers containing fluorinated monomers. [11]

Fluorinated coatings have been used in the applications of architecture, household, leather, metals and so on due to their peculiar performances, such as hydrophobicity, chemical stability, weathering resistance, release properties and so on. Polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) [23] have only limited utilities in coating fields. The high crystalline degree prevents them from dissolving in common solvents and very high baking temperatures are required during their painting process. Recently, fluoropolyacrylates have gained increasing interest for coating systems due to the ease of their synthesis and their desirable properties. They can be prepared by copolymerization of fluoroacrylate with the common acrylate monomers in solution or in aqueous emulsion. The obtained polymers can be cured by ways similar to that of typical polyacrylate coatings under various conditions. It is well known that fog or frost is often formed on a cold surface under humidity conditions. The frost formed on evaporators is now troublesome for heating pumps, coolers and air conditioners because it can drastically decrease the working efficiency in these systems. The utility of antifrosting coatings on the surface of the evaporators is an effective approach to solve this problem. Although both hydrophilic and hydrophobic coatings can be used as antifrosting coatings, hydrophobic coatings are more suitable for use under cold temperature.[12]

A polymer that contains fluorine moieties in the chain exhibits superior chemical and thermal stability, biocompatibility, and extremely low surface energy. Because of these unique properties, many research efforts have contributed to exploring the preparation of fluorinated polymers. Of particular interest are block copolymers containing both fluorinated and nonfluorinated segments. The potential applications of fluorinated block copolymers are quite diverse. For example, they can be used to reduce the surface energy of a bulk material, as a solution state viscosity modifier,

and as a surfactant containing a "CO_2-philic" segment for reactions in supercritical CO_2. It is well known that living polymerization methodology is the most efficient tool for synthesis of well-defined block copolymers.[19]

2.3 Synthesis of Fluorinated Polymers

The fluorochemical compounds remain the most common active igredients for water- and oil repellent purpose. But the price of the fluorinated monomers is relatively high, which limits the application of fluorinated polymer. Up to now, the commercial products of fluoro-acrylate are mostly the random copolymers. The fluorinated units are distributed randomly on the polymer backbone. So the effect of fluorine on the surface energy is constrained. In order to achieve desirable surface property, one approach is to increase the fluorine content of the fluorinated copolymers. The alternative approach is to change the molecular structure and lead to the fluorinated blocks at the end of the molecular chain. By this means, the effiency of fluorine can be increased to a maximum value. The ATRP is a versatile method of synhesizing well-defined polymers.[20]

Until recently, ionic polymerizations(cationic or anionic) were the only living techniques available that efficently controlled the structure and architecture of vinyl polymers.[25] In contrast to ionic synthesis techniques where the growing species are mutually repulsive, radical polymerization suffers from bimolecular termination reactions such as radical recombination and disproportionation. ATRP has opened a new way to synthesize block copolymers. Although the mechanism differ, the underlaying principle for controlling radical polymerization is the same. The main object is to lower the instantaneous concentration of growing radical species by introducing an excess of covalent dormant species that exist in rapid equilibrium with the growth-active radical species. Such a dynamic and rapid equilibrium not only minimizes the probability of the radical bimolecular termination, but also gives an equal opportunity for all living(dormant) chains to propagate via the frequent interconversion between the active and dormant species. These features lead to nearly uniform chain length.

2.3.1 Free Radical Polymerizations

Free radical polymerization (FRP) has many advantages over other polymerization processes. Free radical polymerizations are of significant importance in the industrial sector for a variety of reasons. First, many monomers capable of undergoing chain reactions are available in large quantities from the petrochemical sector [29]. In addition, free radical mechanisms are well understood and extension of the concepts to new monomers is generally straightforward. A third advantage of free radical routes is that the polymerization proceeds in a relatively facile manner: rigorous removal of moisture is generally unnecessary while polymerization can be carried out in either the bulk phase or in solution. However, the major limitation of FRP is poor control over some of the key elements of the process that would allow the preparation of well-defined polymers with controlled molecular weight, polydispersity, composition, chain architecture, and site-specific functionality.

As chain reactions, free radical polymerizations proceed via four distinct processes:

1. *Initiation*. In this first step, a reactive site is formed, thereby "initiating" the polymerization.

2. *Propagation*. Once an initiator activates the polymerization, monomer molecules are added one by one to the active chain end in the propagation step. The reactive site is regenerated after each addition of monomer.

3. *Transfer*. occurs when an active site is transferred to an independent molecule such as monomer, initiator, polymer, or solvent. This process results in both a terminated molecule (see step four) and a new active site that is capable of undergoing propagation.

4. *Termination*. In this final step, eradication of active sites leads to "terminated," or inert, macromolecules. Termination occurs via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation).

The free radical chain process is demonstrated schematically below (Figure 2.5): R· represents a free radical capable of initiating propagation; M denotes a molecule of monomer; R_m and R_n . refer to propagating radical chains with degrees of polymerization of *m* and *n*, respectively; AB is a chain transfer agent; and $P_n + P_m$ represent terminated macromolecules.

Because chain transfer may occur for every radical at any and all degrees of polymerization, the influence of chain transfer on the average degree of polymerization and on polydispersity carries enormous consequences. Furthermore, propagation is a first order reaction while termination is second order. Thus, the proportion of termination to propagation increases substantially with increasing free radical concentrations. Chain transfer and termination are impossible to control in classical free radical processes, a major downfall when control over polymerization is desired.

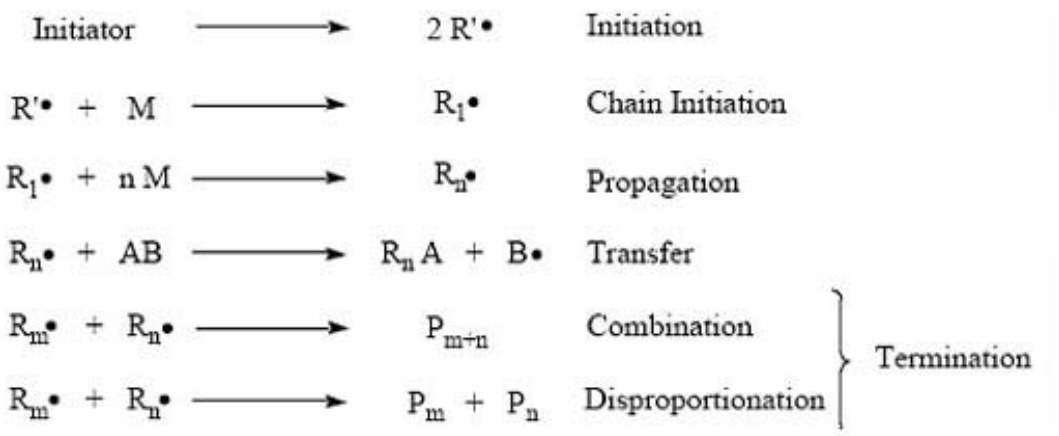


Figure 2.5: Free Radical Chain Process

2.3.2 Controlled / Living Radical Polymerizations

Generally, block copolymers can be prepared in a sequential fashion by the polymerization of one monomer, followed by a second monomer. This is also true for controlled radical polymerizations (Figure 2.5), which permit the synthesis of wide variety of block copolymers and maybe be more versatile than other living polymerization methods

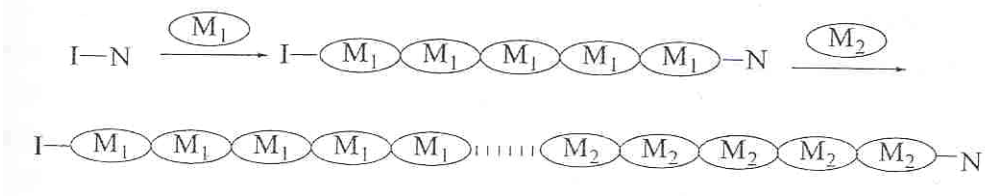


Figure 2.6: Sequential-Controlled Radical Polymerization

Sequential-controlled radical polymerization includes (1) the addition of the second monomer into the polymerization system of the first monomer without any isolation, and (2) the initiation of the polymerization of second monomer using a macroinitiator obtained from controlled radical polymerization of the first monomer. The term controlled/"living" radical polymerization (C/LRP) was initially used to describe a chain polymerization in which chain breaking reactions were absent [30,31]. In such an ideal system, after initiation is completed, chains only propagate and do not undergo transfer and termination. However, transfer and termination often occur in real system. Thus, living polymerization (LP, no chain breaking reactions) and controlled polymerization (CP, formation of well defined polymers) are two separate terms.

A controlled polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality.

Transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected. On the other hand, living polymerizations will lead to well defined polymers only if the following additional perquisites full filled:

-initiation is fast in comparison with propagation

-exchange between species of different reactivities is fast in comparison with propagation

-the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of availability of active centers and mixing.

Well defined polymers [26] may be formed in radical polymerization only if chains are relatively short and concentration of active center (free radicals) is low enough. There is apparent contradiction between these two requirements because usually a decrease of the concentration of radicals leads to higher molecular weights. However, the two conditions can be accommodated in systems with reversible deactivation of growing radicals. The controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weight sufficiently low. This necessitates a relatively high concentration of the initiator, or in other words, low $[M]_o$ / $[I]_o$ ratios. However, when $[I]_o$ is high, since the termination is bimolecular, contribution of termination becomes more significant when a large concentration of radicals $[R^{\bullet}]$ is generated.

Therefore establishing an exchange between dormant and active species is necessary to solve this discrepancy. The concentration of dormant species can be equal to $[I]_o$, and the concentration of momentarily active species to $[R^{\bullet}]$. The total number of growing chains will be equal to $[I]_o$, and radicals would be present at a very low stationary concentration, $[R^{\bullet}]$, and therefore the contribution of termination should be very low.

The three approaches have been used to control radical systems. The best examples of the first approach include stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation transfer polymerization (RAFT) based on photo labile iniferters. The second approach is less common and may be included some organometallic species such as Cr(III) or Al derivatives as well as nonpolymerizable alkenes such as stilbene or tetra thiafulvalene. The last approach can be best exemplified chemistry, via methacrylate monomers [32].

2.3.3 Atom Transfer Radical Polymerization (ATRP)

ATRP is one of the most versatile controlled radical polymerization method [33,34]. This method utilizes a reversible halogen atom abstraction step in which a lower oxidation state metal complex (M_t^n complexed by ligand) reacts with an alkyl halide (R-X) to generate a radical ($R^{\bullet}$), with an activation rate constant (k_a), and a higher oxidation state metal complex (X-M_t^{n+1}/Ligand). This radical then adds monomer to generate the polymer chain (k_p). The higher oxidation state metal can then deactivate

the growing radical to generate a dormant chain and the lower oxidation state metal complex (k_d) as seen in Figure 2.7. The molecular weight is controlled because both initiation and deactivation are fast, allowing for all the chains to begin growing at approximately the same time while maintaining a low concentration of active species. Termination cannot be totally avoided; however, the proportion of chains terminated compared to the number of propagating chains is small [42]. Several metal/ligand systems have been used to catalyze this process and a variety of monomers including styrene, (meth)acrylates, and acrylonitrile have been successfully polymerized [37-39].

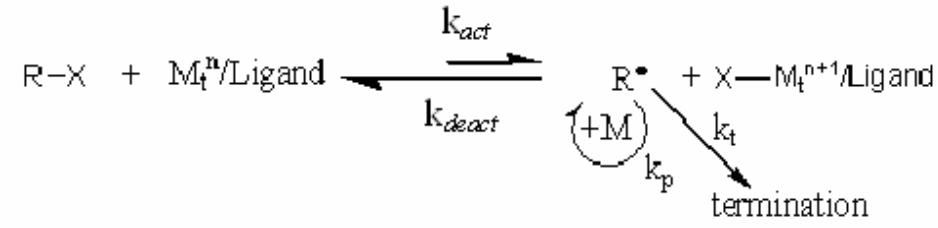


Figure 2.7: Transition Metal Catalyzed ATRP

The rate of ATRP is internally first order in monomer, externally first order with respect to initiator and activator, M_t^n, and negative first order with respect to deactivator, X-M_t^{n+1}. The actual kinetics depends on many factors including the solubility of activator and deactivator, their possible interactions, and variation of their structures and reactivities with concentrations and composition of the reaction medium.

One of the most important parameters in ATRP is the dynamics of exchange, especially the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_d, and also with the concentration of deactivator, [X-M_t^{n+1}]. They, however, increase with the propagation rate constant, k_p, and the concentration of initiator, $[R\text{-}X]_o$. This means that more uniform polymers are obtained at higher conversion, when the concentration of deactivator in solution is high and the concentration of initiator is low. Also, more uniform polymers are formed when deactivator is very reactive and monomer propagates slowly (styrene rather than acrylate) [43].

A wide variety of block copolymers (Figure 2.8) can be prepared by metal-catalyzed controlled radical polymerizations. Most of the block copolymers consist of methacrylates and/or acrylates and/or strene and can be synthesized both via sequential and via controlled radical polymerization using macroinitiators.

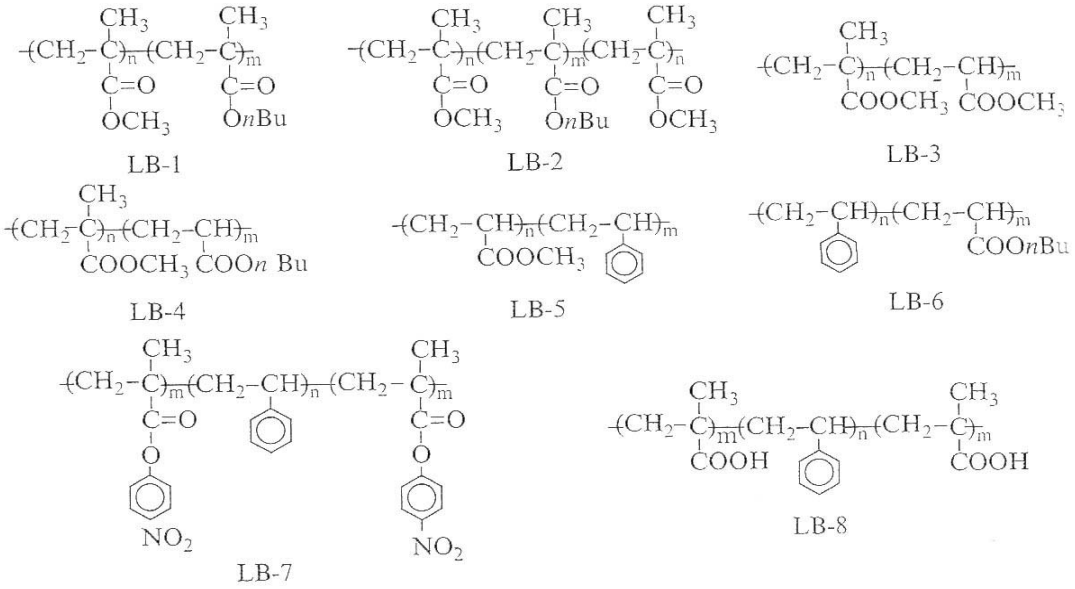


Figure 2.8: Block Copolymers Prepared by ATRP

Controlled radical polymerization of methyl methacrylate(MMA) followed by n-Butyl methacylate (n-BuMA) produces linear AB diblock copolymer LB-1 with narrow molecular weight distrubition. (M_wD, M_w/M_n = 1.2), which can be extented further into ABA triblock copolymer LB-2 with a similar narrow distrubition (M_w/M_n = 1.2) The block copolymers of MMA and MA (methyl acrylate), LB-3 and LB-4 were prepared using catalyst based on nickel, copper or iron complexes. Several acrylate/styrene (St) block copolymers such as LB-5 and LB-6 using a copper-based complex. The ATRP of St was performed using α,α'-dibromo-p-xylene (DBX) as initiator and CuBr/bipyridine (bpy) as catalyst and ligand. PSt with two terminal bromine groups was obtained and succesfully used as macroinitiator in the polymerization of p-nitrophenyl methacrylate (NPMA). The ABA triblock LB-7 was obtained. Hydrolysis of LB-7 in acidic solution produced amphiphilic copolymer LB-8.

Block copolymer can be prepared via controlled radical polymerization using

macroinitiators. In order to avoid the troublesome separation of block copolymers from the homopolymer, the ATRP is generally stopped at lower conversion of the first monomer polymerization in order to ensure one bromine group at each end of the polymer chain.

Fluorine-substitued polymers are as amphiphilic emulsifiers in $scCO_2$ polymerization, the fluorine block being "CO_2-philic" and the conventional organic block being "CO_2-phobic". Thus perfluoroalkyl acrylates and St, which was prepared in $scCO_2$ or in the bulk.

For example, the first block was prepared from the bulk ATRP of St, MA or butyl acrylate (BA). After isolation, purification and characterization, the corresponding polymer was used as macroinitiator in the ATRP of fluorinated alkyl methacrylates, forming diblock copolymers with a hydrocarbon block and a fluorocarbon blcok. Using a difunctional initiator such as DBX, ABA triblck copolymers were obtained as Figure 2.9.

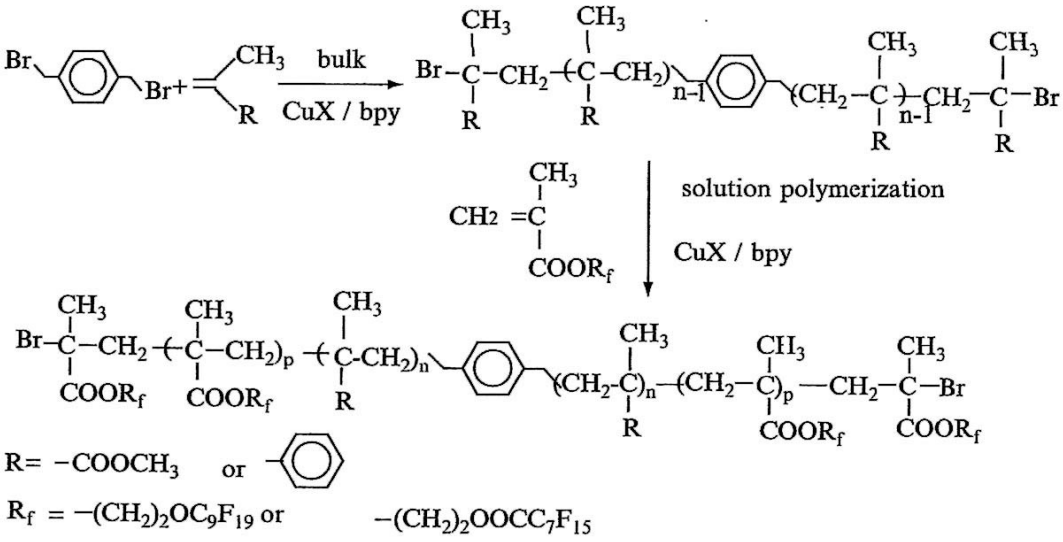


Figure 2.9: Example of Diblock Copolymer via ATRP

Various amphiphilic block copolymers have been synthesized by sequential polymerizations of the protected forms of functional monomers, followed by deprotection.[24] One example is the synthesis of PMA-*b*-poly(acrylic acid), as shown figure 2.10. A diblock copolymer, PMA-*b*-poly(*tert*-butyl acrylate) was

prepared by first polymerizing MA, followed by the growth of *t*BA from the PMA macroinitiator. This diblock was treated in dichloromethane with anhydrous triflic acid (TFA) at room temperature. Selective cleavage of the *tert*-butyl ester group of P*t*BA block occure to produce the amphiphilic block copolymer, PMA-PAA.

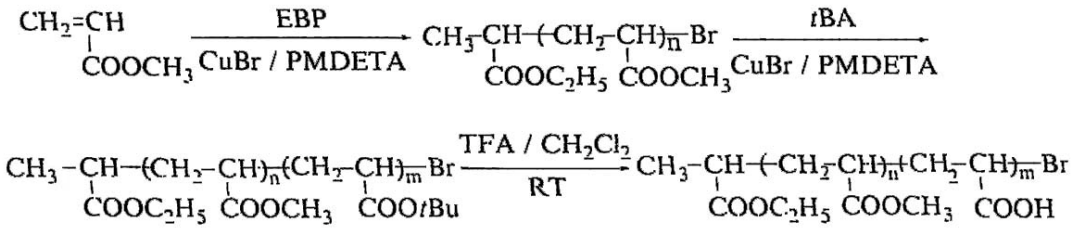


Figure 2.10: Synthesis of PMA-*b*-PAA

2.3.3.1 Monomers

A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq}=k_a/k_d$) determines the polymerization rate.

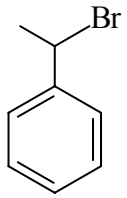
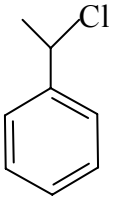
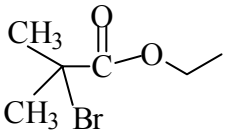
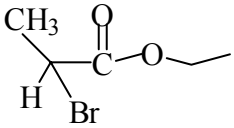
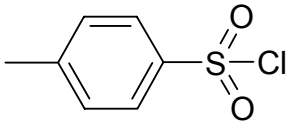
2.3.3.2 Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

Initiators for ATRP must have a halogen (Br or Cl) and a functional group that can stabilize the formed radical, e.g. carbonyl, cyano or phenyl. The initiator is normally chosen so that the structure mimics the structure of the monomer with the aim of making the rate of initiation and propagation equivalent (ki = kp). Different

functionalities can be incorporated in the initiator and a number of functional groups can be tolerated including epoxide, hydroxyl, cyano and lactone. Multifunctional initiators can be used to synthesize more advanced structures such as star polymers.[9] In ATRP, alkyl halides (R-X) are typically used as initiator (Table 2.1) and the rate of polymerization is first order with respect to the concentration of R-X. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best. Fluorine is not used because the C-F bond is too strong to undergo homolytic cleavage.

Table 2.1: The Most Frequently Used Initiator Types in ATRP Systems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methyl methacrylate
 Ethyl-2-bromo propionate	Methyl acrylate and Styrene
 p-toluene sulphonyl chloride	Methyl methacrylate

2.3.3.3 Ligands

Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen

exchange between the metal center and the dormant species or persistent radical. Ligands, typically amines or phosphines, are used to increase the solubility of the complex transition metal salts in the solution and to tune the reactivity of the metal towards halogen abstraction. So far, a range of multidentate neutral nitrogen ligands was developed as active and efficient complexing agents for copper-mediated ATRP, including, bipyridines [43-45] (Figure 2.12), terpyridines [46], phenantrolines[47], picolyl amines [46,47], pyridinemethinamines and tri [43] or tetradentate aliphatic amines [48] including linear and branched amines (2.4). Tridentate and tetradentate ligands generally provide faster polymerizations than bidentate ligands, while monodentate nitrogen ligands yield redox-initiated free radical polymerization. In addition, ligands with an ethylene linkage between the nitrogens are more efficient than those with a propylene or butylene linkage [28].

Linear amines with ethylene linkage like tetramethylethylenediamine (TMEDA), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (Figure 2.11) were synthesized and examined for ATRP as ligands [43]. Reasons for examining of these type of ligands are, they have low price, due to the absence of the extensive π-bonding in the simple amines, the subsequent copper complexes are less colored and since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bpy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates. The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as

- N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA),
- Tetramethylethylenediamine (TMEDA),
- 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA),
- Tris[2-(dimethylamino) ethyl]amine (Me_6-TREN)
- Alkylpyridylmethanimines are also used.

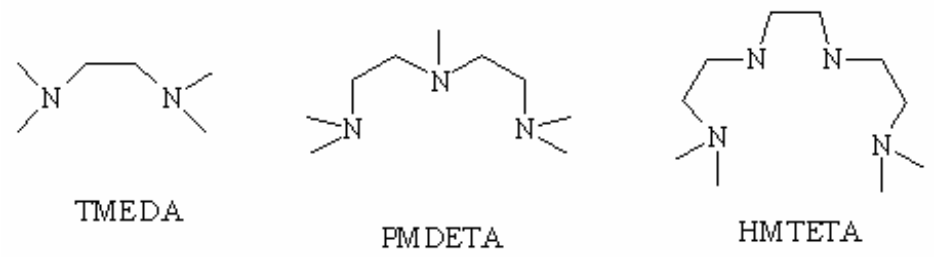


Figure 2.11: Nitrogen Based Ligands

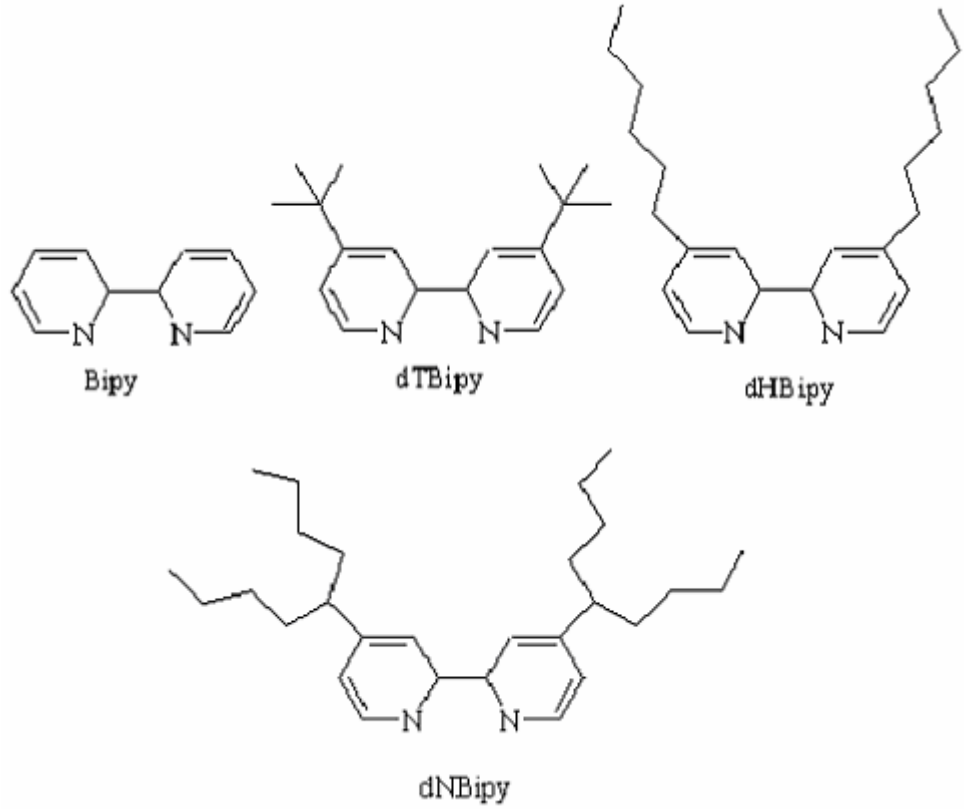


Figure 2.12: Derivatives of 2,2-Bipyridine

Solubility of the ligand and its metal complexes in organic media is of particular importance to attain homogeneous polymerization conditions. The rate of polymerization is also affected by the relative solubilities of the activating and the deactivating species of the catalyst. In heterogeneous systems, a low stationary concentration of the catalyst species allows for a controlled polymerization, but the polymerization is much slower than in homogeneous systems [28]. The ligand with a long aliphatic chain on the nitrogen atoms provides solubility of its metal complexes

in organic solvents. However, the increasing length of the alkyl substituents induces steric effects and can alter the redox potential of the metal center. Any shift in the redox potential affects the electron transfer and the activation–deactivation equilibrium [46].

2.3.3.4 Transition Metal Complexes

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second the metal center should have reasonable affinity toward a halogen and finally that it can complex strongly with the ligand. Third the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

2.3.3.5 Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g. emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers which has attracted attention because of environmental friendliness and cost reduction. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer.

2.3.3.6 Temperature and Reaction Time

The rate of polymerization also determines the rate of polymerization by effecting both propagation rate constant and the atom transfer equilibrium constant. The k_p/k_t ratio increase as a result of higher temperature thus enables us better control over the polymerization. However this may also increase the side reactions and chain transfer reactions. The increasing temperature also increases the solubility of the catalyst. Against this, it may also poison catalyst by decomposition. Determining the optimum temperature; monomer, catalyst and the targeted molecular weight should be taken

into consideration.

2.3.3.7 Kinetics of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator ($X\text{-}M_t^{n+1}$/Ligand).

The rate equation of copper-based ATRP is formulated in discussed conditions and given in (Figure 2.13).

$$Rp = k_{app}\,[M] = k_p\,[R\bullet]\,[M] = k_p\,K_{eq}\,[M]\,[I]_0\,([CuX]/[CuX_2])$$

Figure 2.13: The Rate Equation of Copper-Based ATRP

Figure 2.14 shows a typical linear variation of conversion with time in semi logarithmic coordinates (kinetic plot). Such a behavior indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. However, since termination occurs continuously, the concentration of the Cu(II) species increases and deviation from linearity may be observed [26]. For the ideal case with chain length independent from termination, persistent radical effect kinetics implies the semi logarithmic plot of monomer conversion vs. time to the 2/3 exponent should be linear. Nevertheless, a linear semi logarithmic plot is often observed. This may be due to an excess of the Cu(II) species present initially, a chain length dependent termination rate coefficient, and heterogeneity of the reaction system due to limited solubility of the copper complexes. It is also possible that self-initiation may continuously produce radicals and compensate for termination. Similarly, external orders with respect to initiator and the Cu(I) species may also be affected by the persistent radical effect [49].

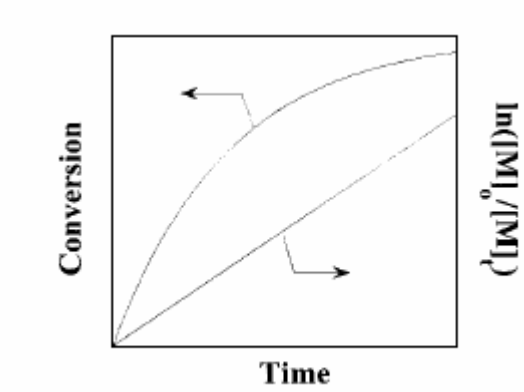


Figure 2.14: Kinetic Plot and Conversion vs. Time Plot for ATRP

Results from kinetic studies of ATRP for styrene (St) [50], methyl acrylate (MA) [51] and methyl methacrylate (MMA) [45,51] under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations. These observations are all consistent with the derived rate law.

It should be noted that the optimum ratio can vary with regard to changes in the monomer, counter ion, ligand, temperature, and other factors [45]. The precise kinetic law for the deactivator CuX_2 was more complex due to the spontaneous generation of Cu(II) via the persistent radical effect [49-50]. In the atom transfer step, a reactive organic radical is generated along with a stable Cu(II) species that can be regarded as a persistent metallo-radical. If the initial concentration of deactivator Cu(II) in the polymerization is not sufficiently large to ensure a fast rate of deactivation (k_d[Cu(II)]), then coupling of the organic radicals will occur, leading to an increase in the Cu(II) concentration.

Radical termination occurs rapidly until a sufficient amount of deactivator Cu(II) is formed and the radical concentration becomes low enough. Under such conditions, the rate at which radicals combine (k_t) will become much slower than the rate at which radicals react with the Cu(II) complex in a deactivation process and a controlled polymerization will proceed. Typically, a small fraction (~5 %) of the total growing polymer chains will be terminated during the early stage of the polymerization, but the majority of the chains (>95 %) will continue to grow successfully. The effect of Cu(II) on the polymerization may additionally be complicated by its poor solubility, by a slow reduction by reaction with monomers

leading to 1,2-dihaloadducts, or from the self-initiated systems such as styrene and other monomers. If the deactivation does not occur, or if it is too slow ($k_p >> k_d$), there will be no control and polymerization will became classical redox reaction therefore the termination and transfer reactions may be observed. To gain better control over the polymerization, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in Figure 2.15.

$M_w/M_n = 1 + ((k_d[RX]_o)/(k_p[X\text{-}M_t^{n+1}])) \times ((2/p)-1)$

p = polymerization yield

$[RX]_o$ = concentration of the functional polymer chain

$[X\text{-}M_t^{n+1}]$ = concentration of the deactivators

k_d = rate constant of deactivation

k_p = rate constant of polymerization

Figure 2.15: Molecular Weight Distribution for ATRP

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

a) For the smaller polymer chains, higher polydispersites are expected to be obtained because the smaller chains include little activation-deactivation steps and also the chain length difference is higher for small polymer chains resulting in little control of the polymerization.

b) For the higher ratios of k_p/k_d, higher polydispersities (molecular weight distributions) are usually obtained resulting in the little control of polymerization.

c) Resulting molecular weight distribution decreases as the concentration of the deactivators increases.

A number of functional groups are not tolerated in ATRP including carboxylic acid and certain ionic groups, which react with the catalyst, thereby impeding the establishment of the equilibrium. However, carboxylic acid groups can be introduced by polymerization of the carboxylic acid salt instead. Other monomers can not be polymerized by this method, because the formed radical is not stabilized enough, which is the case for monomers such as vinyl acetate and halogenated alkenes. The

main problem in using ATRP for syntheses, industrial or otherwise, is removal of the catalyst. The metal catalyst–ligand complex is undesired in the product, as the transition metal induces aging in the polymer, but also for aesthetic (coloration) and toxicological reasons removal is important. Catalyst removal is both difficult and costly, but several methods are presently in use. One procedure is to immobilize the catalyst by having it attached to solid supports during reaction, but this can give loss of control, perhaps due to reduced mobility. Other purification methods include running the raw product on an alumina column, precipitation of polymer and use of an absorbant.

2.4 The Green Chemistry

Rapid technological advances have presented many complex ecological issues. As a result, pollution prevention and waste management represent two of the most profound challenges of the 21st century. The proliferation of the use of organic solvents, halogenated solvents, and precious water in manufacturing and processing industries, such as electronics, pharmaceuticals, dyes, and coatings, has created the right atmosphere for the creation and development of environmentally responsible and energy efficient processes. Polymer industries utilize large amounts of volatile organic compounds as reaction media to prepare polymers. In order to minimize the impact of the chemical industry on human health and the environment, the use of hazardous substances in chemical processes and final products should be reduced or eliminated. The promising application of supercritical (SC) fluids as alternative solvents, reactants or catalysts for chemical processes could be an important contribution to a cleaner environment. In many instances, the unique properties of SC fluids might be an advantage over traditional solvents. For example, the physicochemical properties (density, viscosity, diffusivity, dielectric constant, solubility parameter, etc.) of an SC fluid can be adjusted from gas-like to liquid-like values by variation of pressure and temperature. [64] This pollution-prevention approach is much more sustainable and appropriate than the “end-of-pipe” approach embodied in many waste-management methods.

2.4.1 Supercritical Carbon Dioxide and Its Properties

Carbon dioxide is a natural solvent (phase diagram in Figure 2.16) that could replace water and many other solvents in many applications. CO_2 attains its supercritical state at near-ambient temperature (Tc = 31.2 ^oC) and a relatively moderate pressure. (Pc = 7.38 Mpa, 73.8 bar) [64] CO_2 is advantageous because it is abundant, inexpensive, nontoxic and nonflammable, tunable physico-chemical properties and can be completely and easily removed from products as on the release of pressure it returns to a gas thus leaving negligible solvent residues, no production of unstable end groups, elimination of expensive energy-intensive heating and fluorination steps, substantially inert towards chain transfer reactions [61].

Supercritical CO_2 ($scCO_2$) offers many mass transfer advantages over conventional organic solvents owing to its gas-like diffusivity, low viscosity, and surface tension.

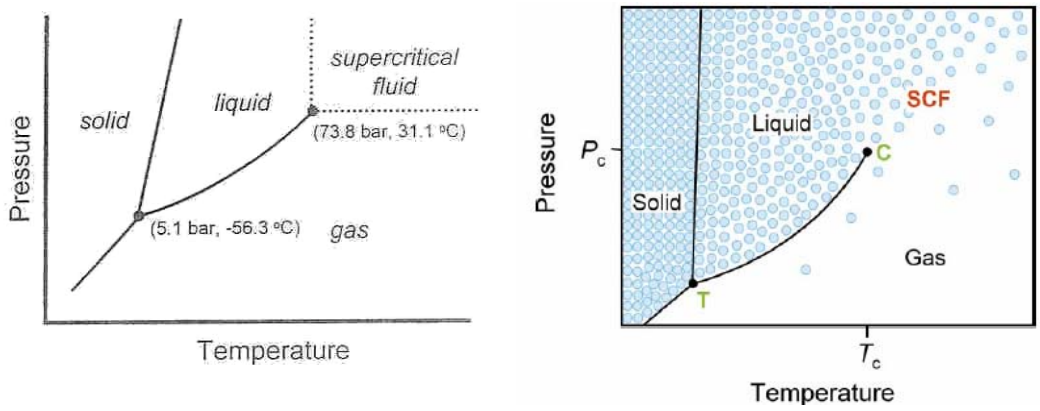


Figure 2.16: Carbon Dioxide Phase Diagrams

It has been proposed as a 'green' alternative to traditional organic solvents because it is a volatile organic chemical allowed in food or pharmaceutical applications[64]. CO_2 is also naturally occurring and readily available; it can be found in natural reservoirs and is a by-product from the production of ammonia, ethanol, hydrogen, and natural gases. CO_2 is routinely handled on a commercial scale using pressurized and refrigerated tanks for storage and processing liquid CO_2 and cylinders for compressed CO_2 gas. When released to the atmosphere, liquid CO_2 leaves no residue to contaminate either the environment or personnel. Processes that use CO_2 do not add directly to the greenhouse effect (global warming caused by the entrapment of

heat into the atmosphere by gases that are emitted into the environment) but rather aid in the reduction of emitted CO_2 . Most of the CO_2 sold today (82%) is a by-product from other industries. In addition to environmental benefits, CO_2-based processes can also be more energy efficient than those based on water or conventional solvents. The low heat of vaporization of CO_2 significantly reduces the energy costs that are associated with water-intensive processing industries and also eliminates the inevitable contamination problems associated with the pollution of water effluent streams. The main problem with $scCO_2$ is its low dissolving power toward most polar compounds, and high molecular-mass polymers. Despite CO_2 is a good solvent for many vinyl monomers, it is a poor solvent under relatively mild conditions ($P < 35MPa$, $T < 100$ C) for high molar mass polymers with the exclusion of amorphous fluoropolymers, polysiloxanes, and polyether-polycarbonate copolymers. Hence free radical polymerization of high molar mass polymers can be achieved in $scCO_2$ only through heterogeneous processes. This means that to exploit successfully the aforementioned technological and environmental advantages of dense carbon dioxide, a suitable surfactant must be added to the polymerization medium to allow the stabilization of the polymer particles. Although the use of dense CO_2 (liquid CO_2 or $scCO_2$) in a process may add some technical difficulties; mainly because it requires high-pressure equipment, the vapor pressure of CO_2 at room temperature being more than 60 bar. [61]

Having a low dielectric constant and low polarizability power, CO_2 displays weak intermolecular interactions such as van der Waals forces. However, CO_2 has a large quadrupole moment and has Lewis acidity; these properties together contribute positively to the solubility parameter and allow interactions of CO_2 with several functional groups.

Molecules having low cohesive energies, such as certain fluorocarbons and fluoroethers, siloxanes, and polycarbonates are widely known CO_2-soluble compounds. As a result, processes in $scCO_2$ often require the aid of a surfactant to ensure dispersion of the desired solute in the continuous phase.

Most of the recent research in the area deals with such compounds, aiming at the synthesis of novel surfactants to overcome the problem of CO_2 solubility. Major concentration is on the synthesis of polymeric and small-molecule surfactants that contain a CO_2-philic segment, compatible with the supercritical phase, and a CO_2-

phobic segment, consisting of CO_2-insoluble compounds. The benefits and drawbacks of $scCO_2$ have been stated explicitly, but applications of $scCO_2$ have not become sufficiently extensive yet because the majority of the commercially available surfactants have very low solubility in CO_2 and many are not effective in forming stable micelles.[65]

2.4.2 $scCO_2$ Applications

The highly versatile nature of CO_2 has been exploited in numerous industries and applications. CO_2 has been used for decades for food freezing and for pH control in the textile and pulp-and-paper industries. Commercialized in the 1970s as a natural extractant in decaffeination processes, coffee, tea, and spice industries have used $scCO_2$ to replace dichloromethane and ethylene dichloride. In 1997, Ford Motor Company switched some of their bumper-coating processes from hazardous solvent-based paints and primers to utilize CO_2 technology. More recently, Micell Technologies has commercialized an innovative process wherein molecular engineered surfactant molecules, combined with CO_2 , provide an environmentally friendly alternative to the traditionally hazardous solvents used today, such as perchloroethylene (PERC).

2.4.3 Dispersion Polymerization in $scCO_2$

Interesting applications of $scCO_2$ include surfactant-aided heterogeneous polymerizations, such as dispersion and emulsion polymerizations. As most conventional monomers are soluble in $scCO_2$, dispersion polymerization is usual, whereas there are only a few reports on the inverse emulsion polymerization of acrylamides. The role of the surfactant is to absorb or chemically attach to the surface of the growing polymeric particles and prevent the particles from aggregating by steric stabilization. One key issue in a successful dispersion or emulsion polymerization in $scCO_2$ is the choice of the appropriate surfactant.[62]

In 1994 DeSimone et al. reported the dispersion polymerization of methyl methacrylate (MMA) in $scCO_2$ stabilized by a fluoroacrylate homopolymer, the poly(1,1-dihydroperfluorooctyl acrylate). A number of other fluorinated and siloxane polymers have also been identified as effective in $scCO_2$ under the form of block, graft or pseudo-graft copolymers and of reactive macromonomers .

Most of tested surfactants are expensive and/or need a complex procedure to be synthesized and this has a negative fall-out on the applicative perspective of dispersion polymerization in $scCO_2$.[61]

Dispersion polymerization in the presence of suitable steric stabilizers is the process of choice to obtain acceptable yields and molar masses.Dispersion polymerization is a heterogeneous reaction process, and begins with the formation of a homogeneous mixture due to the solubility of both the monomer and the initiator in the continuous phase when using a suitable stabilizer. Polymerization takes place initially through a solution phase reaction to produce oligomeric radicals. When the growing oligomeric radicals reach a critical chain length, the chains become insoluble in the continuous phase and precipitate from the solution. To achieve a successful dispersion polymerization, and to prevent flocculation of particles in $scCO_2$, a surface active stabilizing molecule must be used. Its role is to physically adsorb or chemically attach to the surface of the polymeric particles and form stable nuclei. The effectiveness of a stabilizer is governed by two factors; firstly there must be sufficiently strong anchoring to the polymer particle, and secondly the soluble segment must be chain extended into the continuous phase thus facilitating a negative steric interaction between particles (e.g. of sufficient solvation and chain length). These factors can be controlled by synthetic variation of both the composition and architecture of the stabilizers for the polymerization reactions in $scCO_2$ medium. Stabilizers can be classified as either CO_2-philic or CO_2-phobic based on their solubility characteristics. In order to perform dispersion polymerizations, amorphous fluoropolymers and polysiloxanes are used because of their solubility in $scCO_2$, while most other polymers are insoluble in $scCO_2$. As such, these polymers are described as CO_2-philic and CO_2- phobic, respectively.

There are other fluorinated and siloxane polymers which have been shown to be effective stabilizers for dispersion polymerization in $scCO_2$. Additionally, poly(dimethylsiloxane monomethacrylate) (PDMSMMA) macromonomer has been employed extensively in the polymerization of MMA. However, macromonomers have the disadvantage of being copolymerized into the resultant product. Alternatively, polymerization can be achieved by the use of block or graft copolymers as effective stabilizers with one section being 'CO_2-philic' (usually

fluorinated and siloxane based) and the other section being 'CO_2-phobic'. The block size or the length of the grafted part has been shown to influence the steric stabilizing properties, with an appropriate balance being required to obtain an effective dispersion. Dispersion polymerization of a very wide range of vinyl monomers has been reported, including 2-hydroxyethyl methacrylate, vinyl acetate, acrylonitrile, N-vinyl pyrrolidinone, glycidyl methacrylate, and copolymers of MMA. In dispersion polymerization, although fluorine containing acrylate homopolymers provide sufficient stabilization to produce micron-size polymer particles in scCO_2, these homopolymers have several drawbacks such as limited solubility in hydrocarbon solvents (which makes characterization difficult) and relatively high cost. To reduce the amount of expensive fluorinated acrylate monomer, fluoroacrylate block or graft copolymers are prepared by using different comonomers.The use of fluorinated random copolymers as stabilizer has several advantages for successful dispersion polymerization in scCO_2 since random copolymers are easily synthesized by radical polymerization in comparison with block or graft copolymers which undoubtedly are more complicated to synthesize via 'controlled' radical polymerization or living anionic polymerization.[64]

The polymerization of tetrafluoroethylene to PTFE in CO_2 is of particular importance because it emphasizes a safe new route to fluorolefin polymers. Conventional routes to fluoropolymers typically employ aqueous or chlorofluorocarbon (CFC) based solvent systems that do not have readily abstractable hydrogen atoms, which leads to premature chain termination. Aqueous based processes also generally produce carboxylic acid and acid fluoride end groups that can only be removed by expensive steps, such as high-temperature hydrolysis or fluorination. The Montreal Protocol banned the use of CFCs because of their deteriorating effect on the Earth's ozone layer. Fluoropolymers and siloxanes represent a very small fraction of the industrially important polymers; therefore, surfactants are needed to broaden the efficacy of liquid and supercritical CO_2 to include the synthesis of other polymers using heterogeneous polymerization methods. Just as surfactants are important to aqueous technologies, surfactants are also the key to extractions, coatings, cleaning, drug delivery, and heterogeneous polymerizations in CO_2 . The lack of commercially available CO_2 surfactants led researchers to develop CO_2 soluble amphiphilic block-

copolymer surfactants that incorporated "CO_2 philic" fluorinated or siloxane components and "CO_2 phobic" hydrophilic or lipophilic components. As a result of the inherent incompatibility of the fluorocarbon monomers with other synthetic methods, controlled free radical polymerization techniques were the first to be employed for the synthesis of the amphiphilic block copolymers for use in CO2-based systems. Because of the insolubility of most fluoropolymers in common organic solvents and the presence of some special features in several fluorinated monomers (e.g. two acidic hydrogens on the methylene adjacent to the ester group in 1,1,2,2-tetrahydroperfluorooctyl acrylate (TAN), controlled free radical polymerization methods appeared to be the most versatile available. Specifically iniferter polymerization and atom-transfer radical polymerization (ATRP) techniques were implemented for the synthesis of the block copolymers. The iniferter technique has been used to synthesize a wide range of hydrophilic, lipophilic, and fluorocarbon polymers including poly(2-dimethylaminoethyl methacrylate) (PDMAEMA), polystyrene (PS), poly(vinyl acetate) (PVAc), poly(1,1-dihydroperfluorooctyl acrylate) (PFOA), and 1H,1H-perfluorooctyl methacrylate (PFOMA). While ATRP is not as widely applicable to as many monomers as the iniferter technique, ATRP does give much more controlled and well-defined polymers. ATRP has been shown to be effective in synthesizing polymers derived from acrylates, methacrylates, and styrenics as well as fluorocarbon monomers such as FOMA, and TAN. Additionally, Xia et al. recently demonstrated the synthesis of PFOA using ATRP in scCO2 . Several hydrocarbon-fluorocarbon diblock copolymers synthesized by these techniques are listed in Table2.2. [64]

Table 2.2: Hydrocarbon – Fluorocarbon Diblock Copolymers

Hydro-carbon block	M_n [kgmol^{-1}]	PDI	Fluoro-carbon block	M_n [kgmol^{-1}]	Techniques
PS	3.7	1.7	PFOA	39.8	Iniferter
PS	6.6	1.8	PFOMA	42.3	Iniferter
PVAc	4.4	1.6	PFOA	43.1	Iniferter
PMMA	8.1	1.3	PFOMA	55.9	ATRP
P(*t*BuAc)	5.0	1.6	PFOMA	52.6	ATRP
PHEMA	4.0	1.5	PFOMA	40.0	ATRP

2.5 Contact Angle of Liquid Drops on Solids

2.5.1 Theory of Contact Angles

The surface tension of solids, especially polymers with a low surface free energy cannot be measured directly because of elastic and viscous restrains of the bulk phase, which necessitates the use of indirect methods. Most solids are incapable of adjusting to such equilibrium conformations and in practice their surface structure will be largely frozen-in record of an arbitrary past history, where some imperfections, humps and cracks are present. Thus, the laws of capillarity of liquids cannot be applied to solids. The only general method is the rather empirical method of estimating the solid surface tension from that of the contacting liquid. If we consider a liquid drop resting on a solid surface as shown in Figure 2.17, the drop is in equilibrium by balancing three forces, namely, the interfacial tensions between solid and liquid, SL; between solid and vapor, SV; and between liquid and vapor, LV. The contact angle, θ, is the angle formed by a liquid drop at the three-phase boundary where a liquid, gas and solid intersect, and it is included between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid, at the point of intersection.

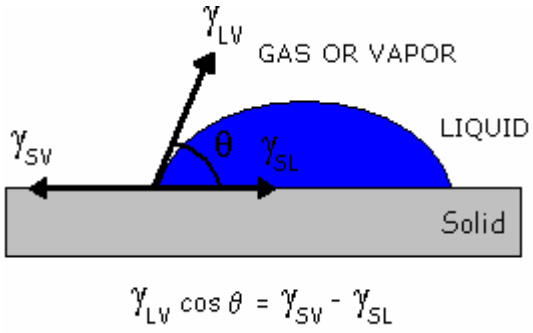


Figure 2.17: Vectorial Equilibrium for a Drop of a Liquid Resting on a Solid Surface

The contact angle is a quantitative measure of wetting of a solid by a liquid. Unless it is very volatile, any liquid (including liquid metals such as mercury) having a low viscosity can be used as the liquid of the drop. Low values of θ indicate a strong liquid-solid interaction such that the liquid tends to spread on the solid, or wets well,

while high θ values indicate weak interaction and poor wetting. If θ is less than 90°, then the liquid is said to wet (or sometimes partially wet) the solid. A zero contact angle represent complete wetting. If θ is greater than 90°, then it is said to be non-wetting.

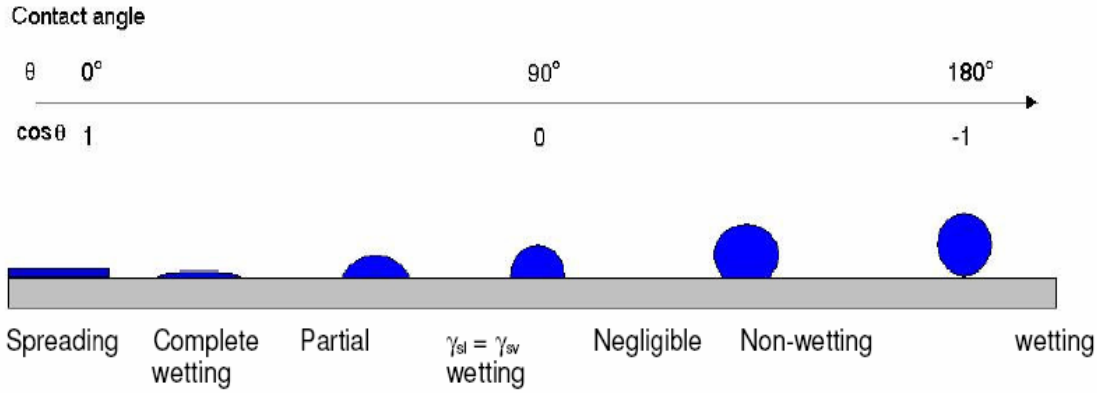


Figure 2.18: Wettability of a Surface by a Liquid

From point of view, if the solid has a low-energy surface, it attracts the molecules of the liquid with less force than the liquid molecules attract one another. Therefore, molecules in the liquid next to the surface have a weaker force field than in the liquid surface, so that the liquid molecules at the interface are pulled more strongly into the bulk of the liquid than they are by the solid. There is a tension in the layer adjacent to the solid, and the liquid molecules are somewhat seperated, owing to the one-sided force field. The situation is analogous to the behavior of a drop of one liquid on another immiscible liquid, the drop liquid having a higher surface tension than that of the lower liquid (but not equivalent because of the mobility of surface molecules at the interphase region between two immiscible liquids).

T.Young was the first to describe contact angle equilibrium, in 1805.The vectorial summation of forces at the three-phase intersection point (so-called *three-phase contact point*) gives

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \qquad \textbf{(2.1)}$$

where γ is the surface tension (or surface free energy) term. If [$\gamma_{SV} > (\gamma_{SL} + \gamma_{LV})$]

which shows the presence of a high surface energy solid, then Young's equation indicates ($\cos \theta = 1$), corresponding to ($\theta = 0$), which means the complete spreading of the liquid on this solid.[69]

2.5.2 Industrial Applications of Contact Angles

Measurements of contact angles provides a better understanding of the interactions between solids and liquids, or between immiscible liquids. Although it is a difficult task to measure the contact angle properly on solids, a large body of reliable data has been accumulated and a vast literature exists correlating contact angle data with surface tension of solids. The interactions between solids and liquids play a key role in understanding the chemical and physical processes in many industries. The adhesion between different composite structures (glass-metal, leather-fabric, wood-paper) and the wetting of adhesive on a substrate can be accessed by contact angle measurements. The determination of θ is very important in the paints and coatings industries. The effectiveness of the coating formulation and the coating process, for example a car body coating, can be accessed by measuring the hydrophobicity of the lacquer surface. The advent of new, environmentally friendly water-based coatings and inks started new research in the paper industry to improve ink performance. Adhesion of inks to polymeric food packaging film products also benefits from surface chemistry. As an example, all materials involved in an offset printing process need to have a certain surface free energy in order to attain optimum printing quality, so contact angle measurements are required at many steps in the printing process. On the other hand, composite materials made of reinforcing fibers and polymeric (resin) matrix systems have replaced many of the traditional metals and other heavier and weaker materials, and have begun to be used in a wide range of products in the aerospace, automotive and sporting goods industries. Using contact angle measurements, it is possible to optimize the adhesion between the fiber and resin matrix system, and to find the right formulation of the resin matrix with proper wetting properties against the fiber. In the textile industry, everything from carpet fibers to surgical gowns involves surface treatments such as anti-static or anti-strain coatings applied to the textile material to provide protection. The wettability of single fibers or fabrics as well as their hydrophobicity and washability can be checked by

contact angle measurements. The medical, pharmaceutical and cosmetic industries also use contact angle measurements in their research and quality control laboratories. Surface-modified biomaterials are being employed to created disposable contact lenses, catheters, dental prosthetics and body implants; however they must be biocompatible, that is, they should not be rejected by the human body. Thus, contact angle measurements are necessary in all wettability and biocompatibility studies.[69]

2.5.3 Measurement of Contact Angles

Measurement of contact angles appears to be quite easy when first encountered, but the substrate is not prepared properly and very pure liquids are not used while forming drops and if some important practical issues during measurement, such as drop evaporation, the location of the needle in the drop, and maintaining a sharp image, are not considered, then incorrect and generally useless contact angle results can be obtained, which may be used as evidence for false thermodynamical conclusions.

The measurement of a single static contact angle to characterize the solid-liquid interaction is not adequate because, in practice, there is no single equilibrium contact angle, θ_e, on a solid surface. There may be a range of static contact angles, depending on the location of the drop and on the application type of the measurement. Static contact angle is the contact angle when all participating phases gas, liquid, solid have reached their natural equilibrium positions and the three phases line is not moving anymore.[70] Experimentally, only two types of contact angle measurement technique are standardized:

1- When a liquid drop is formed by injecting the liquid from a needle connected to a syringe onto a substrate surface, it is allowed to advance on the fresh solid surface and the measured angle is said to represent the *advancing contact angle*, θ_a, (it should be noted that the stainless steel needle must be kept in the middle of the drop during measurement and the needle may be coated with paraffin wax in order to prevent climbing of some strongly adhering liquids, such as water.)

2- The receding contact angle, θ_r, can be measured when a previously formed sessile drop on the substrate surface is contracted by applying a suction of the drop liquid

through the needle. Precise measurement of θ_r is very difficult because of the drop evaporation effect. These contact angles fall within a range where the advancing contact angles approach a maximum value and receding angles approach minimum value ($\theta_a > \theta_r$).[69]

2.5.4 Contact Angle Hysteresis

Contact angle hysteresis is the difference between the advancing and receding contact angles:

$$H \equiv \theta_a - \theta_r \qquad \textbf{(2.2)}$$

Hysteresis of the contact angle results from the system under investigation not meeting ideal conditions. In order to apply Young's equation, the solid should be ideal: it must be chemically homogeneous, rigid, flat at an atomic scale and not perturbed by chemical interaction or by vapor or liquid adsorption. If such an ideal solid surface is present, there would be a single, unique contact angle. On the contrary, it is common to find contact angle hysteresis on practical non-ideal surfaces, in the region of 10^o or larger; and 50^o or more of hysteresis has sometimes been observed. In general, there appear to be five causes of contact angle hysteresis. Surface roughness and microscopic chemical heterogeneity of the solid surface are the most important ones, and the others such as drop size effect, molecular reorientation and deformation at the solid surface are less important.[69] When wetting with water the hydrophobic regions will repel the water and the hydrophilic regions will attract the water. Thus when advancing in a hydrophobic region the contact angle increases (the solid tries to limit the area touched by water) and similarly when receding in a hydrophilic region the contact angle decreases (the solid tries to hold on to the water). From this analysis it can be seen that with water advancing angles characterize hydrophobic regions and receding angles characterize hydrophilic regions.

2.5.4.1 Hysteresis due to Molecular Orientation and Deformation on Solid Surface

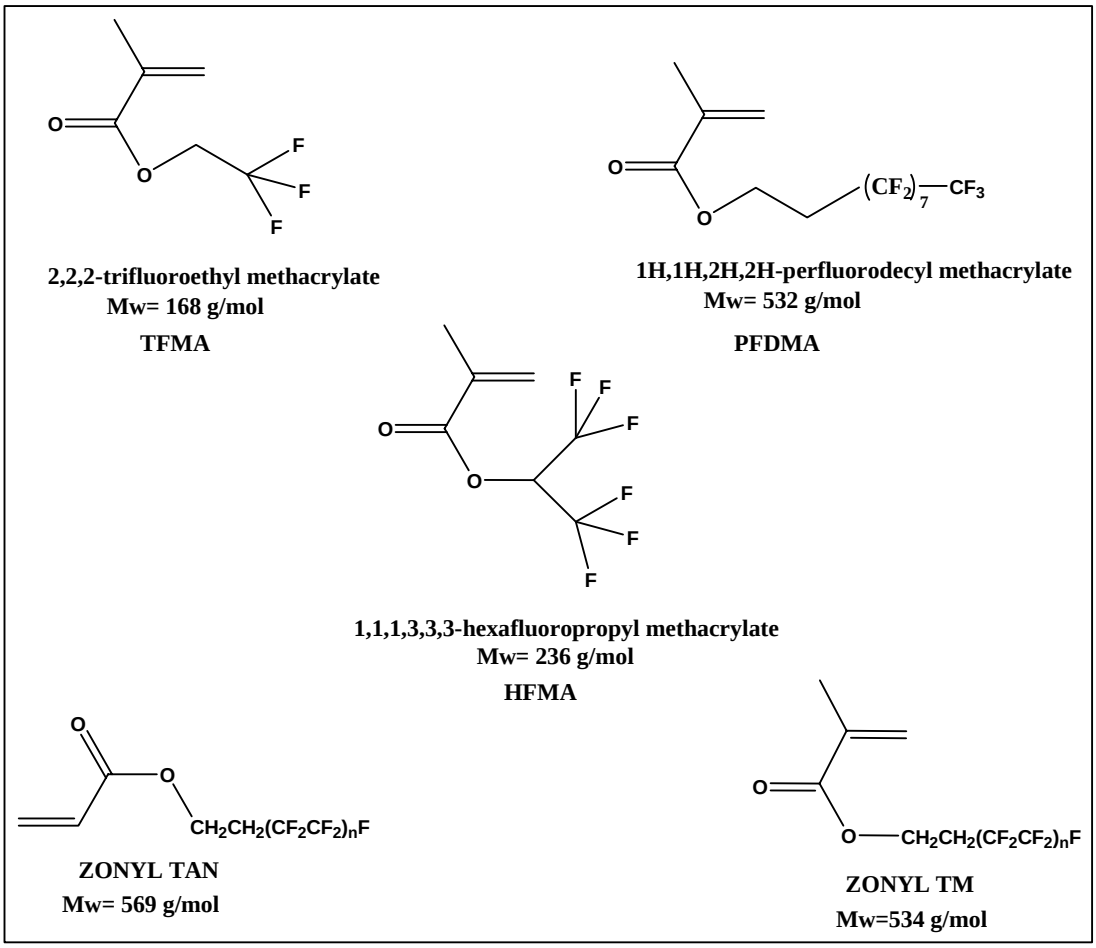
This type of hysteresis often occurs with polymer surfaces. Molecular reorientation in the polymer surface, under the influence of the contacting liquid phase, takes place especially if the polymer has polar or hydrogen-bonding chemical groups in its structure. The terms *surface reconstruction* or *surface reorientation* are also employed. As an example, the hydroxyl groups in a polymer backbone chain are buried away from the air phase for a polymer-air interface, but when a water sessile drop is formed on the polymer surface, the hydroxyl groups turn over to form hydrogen bonds with water. This movement results in reorientation of the surface under test and can be detected by the time-dependent change in contact angle. Such a change does not necessarily require long-range segmental motion but can be achieved by relatively simple short-range motion such as rotational motion segments at the surface. It is obvious that the types of atoms or groups in aparticular polymer chain in bulk do not determine the surface properties, but the types of atoms or groups actually existing at the top of the surface determine the surface-wetting properties.

3. EXPERIMENTAL PART

3.1 Chemicals

Copper (I) bromide (CuBr, 98%), Copper (II) bromide ($CuBr_2$, 99%, anhydrous), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 99%), *tert*-Butyl Acrylate (*t*BA, 99%), Methyl 2-bromopropionate (MBrP, used for tBA, 99%), Methyl methacrylate (MMA, 99%), Ethyl 2-bromoisobutyrate (EBrB, used for MMA, 99%) were purchased from Acros Organics Co. Benzoyl peroxide (BPO, %77) was purchased from Fluka. Fluoroalkyl acrylate (TAN), Fluoroalkyl methacrylate (TM), were purchased from DuPont as sold under the tradename Zonyl® TAN and Zonyl® TM respectively. (Figure 3.1) Tetrahydrofuran (THF), Acetone, Anisole, Toluene, Chloroform ($CHCl_3$), Methanol (MeOH), Dichlorometane (CH_2Cl_2) were purchased from J.T. Baker Co. All reagents were used without further purification.

2,2,2-trifluoroethyl methacrylate (TFMA), 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFMA) and 1H,1H,2H,2H-perfluorodecyl methacrylate (PFDMA) were purchased from Apollo Scientific Ltd. and passed through basic alumina column to remove inhibitors before use. All liquid components were nitrogen bubbled prior to placement into the reaction flask.



Weight Percentages of Components in Products

Fluoroalkane Chain	*Zonyl® TM* (Avg. n = 8.2)	*Zonyl® TA-N* (Avg. n = 9.0)
C_4F_9	4 max.	—
C_6F_{13}	35 ± 3	6 max.
C_8F_{17}	30 ± 3	50 ± 3
$C_{10}F_{21}$	17 ± 2	29 ± 2
$C_{12}F_{25}$	8 ± 1	11 ± 2
$C_{14}F_{29}$ and higher	6 max.	4 max.

Figure 3.1: Fluorine Containing Monomers

3.2 Homopolymerization Procedures by ATRP

3.2.1 Polymerization of *tert*-Butyl Acrylate (*t*BA)

A typical ATRP procedure was performed as follows for run PP-1. CuBr (1.1 mmol) and $CuBr_2$ (0.11 mmol) as catalysts were placed in a 48 ml of flask which contained a side arm with Teflon valve sealed with a Teflon stopper equipped with a magnetic stirring bar. Then the flask was deoxygenated by vacuum-thaw-nitrogen cycles for three times. MBrP (22 mmol) as an initiator, *t*BA (55 mmol) as a monomer, acetone (2 ml) as a solvent, PMDETA (1.2 mmol) as a ligand were added to the flask. Then the flask was replaced in thermostatically controlled oil bath at 60 ^{o}C. Stirring rate was applied as 400 rpm. After 150 min, subsequently the dark green polymerization mixture was diluted with THF and MeOH in order to terminate, and then passed through the neutral alumina column to remove the catalyst, and precipitated in cold MeOH:DI water (50:50 v/v). After filtration, polymer was dissolved in CH_2Cl_2 and extracted in three times with DI water (25 % of CH_2Cl_2). Organic phases were collected and dried with anhydrous sodium sulfate (Na_2SO_4). After filtration of mixture, CH_2Cl_2 was evaporated then dried overnight in high vacuum, pale yellow rubbery solid was received. The isolated P*t*BA's were used as macroinitiators for the synthesis of block copolymers.

3.2.2 Polymerization of Fluorine Containing Monomers

A typical ATRP procedure was performed as follows for run PP-3. CuBr (0.4 mmol) as catalyst was placed in a 48 ml of flask which contained a side arm with Teflon valve sealed with a Teflon stopper equipped with a magnetic stirring bar. Then the flask was deoxygenated by vacuum-thaw-nitrogen cycles for three times. EBrB (0.4 mmol) as an initiator, TFMA (2 mmol) as a monomer were added into the flask. Toluene (1 ml) and PMDETA (0.4 mol) as a ligand. Then the flask was replaced in thermostatically controlled oil bath at 400 rpm stirring rate and given temperature. After 48 hours, subsequently the dark green polymerization mixture was diluted with $CHCl_3$ and MeOH to terminate, then extracted in three times with DI water (25% of $CHCl_3$). Organic phases were collected and part of excess $CHCl_3$ was evaporated then remaning solution was precipitated into cold MeOH:DI water (50:50 v/v), pale white solid was received.

Figure 3.2: 48 ml Reaction Flask

3.2.3 Polymerization of methyl methacrylate (MMA)

A typical ATRP procedure was performed as follows for run HP-7. CuBr (0.467 mmol) as a catalyst was placed in a 48 ml of flask which contained a side arm with Teflon valve sealed with a Teflon stopper equipped with a magnetic stirring bar. Then the flask was deoxygenated by vacuum-thaw-nitrogen cycles for three times. EBrB (0.467 mmol) as an initiator, MMA (0.1 mol) as monomer, PMDETA (0.467 mmol) as ligand and toluene (5 ml) as solvent were added into the flask. Then the flask was replaced in thermostatically controlled oil bath at 80 ^{o}C. Stirring rate was applied 400 rpm. After 80 min., subsequently the dark green polymerization mixture was diluted with THF and MeOH to terminate, then passed through the neutral alumina column to remove the catalyst, and precipitated in cold MeOH:DI water (50:50 v/v). After filtration, polymer was dried for 24 h in a vacuum oven at 40 ^{o}C.

3.3 Block copolymerization procedures by ATRP

Solid materials such as macroinitiators and CuBr were placed in a 48 ml of flask which contained a side arm with Teflon valve sealed with a Teflon stopper equipped with a magnetic stirring bar. Then the flask was deoxygenated by vacuum-thaw-nitrogen cycles for three times. Ligand, solvents and appropriate monomers (given in Table 4.2) were added, respectively. Then the flask was replaced in thermostatically controlled oil bath at a given temperature. After given time, polymerization mixture was diluted with $CHCl_3$ and MeOH, then extracted in three times with DI water (25% of $CHCl_3$). Organic phase was collected then part of excess $CHCl_3$ was

evaporated and remaining solution was precipitated into cold MeOH:DI water (50:50 v/v). After filtration, polymer was dried for 24 h in a vacuum oven at 40 ^{o}C. The pale white solid was received.

3.4 Copolymerization Procedures by Free Radical Polymerization

3.4.1 Methyl Methacrylate and Fluoroalkyl (Meth)acrylate Polymerizations in $scCO_2$ Medium

The polymerization reactions were carried out in a 30 mL stainless steel reactor equipped with an ISCO 260D automatic syringe pump (266 ml capacity, 0.001-107 ml/min flow rate, max 7500 psi : 517 bar). The system was purged for 15 min with CO_2 (analytical grade, 99% from Karbogaz) to remove oxygen. The reactor was charged with MMA (Table 4.3) as a monomer, the desired amounts of BPO as initiator and fluoroalkyl acrylate (TAN) or fluoroalkyl methacrylate (TM) as co-monomer were added to the reactor. Then automatic syringe pump was used to pressurize the reactor with CO_2 to 200(±10) bar, and the reaction mixture was heated to the desired temperature in a heating jacket. As the reaction vessel was heated, the remaining CO_2 was added to the system, until the desired pressure was reached. At the end of the reactions in desired time, CO_2 was vented slowly from the reactor and bubbled through methanol in order to collect any polymer particles which sprayed out during the venting process, then the reactor was cooled in an ice bath. The solid polymer product was then removed from the reactor. The obtained polymer was dried under vacuum, and the conversion was determined gravimetrically.

Figure 3.3: $scCO_2$ System in GYTE Lab. and Polymers

3.4.2 Methyl methacrylate and Fluoroalkyl (Meth)acrylate Polymerizations in Solution

BPO as initiator and toluene were placed in a 250 ml flask which contained a side arm with Teflon valve sealed with a Teflon stopper equipped with a magnetic stirring bar. Methyl methacrylate as monomer and fluoroalkyl acrylate (TAN) or fluoroalkyl methacrylate (TM) were added in to flask (Table 4.3). Then the flask was replaced in thermostatically controlled oil bath at given temperature. After given time, polymerization was ended up with THF and MeOH. After, polymer mixture was precipitated into MeOH:DI water (50:50 v/v), filtered and dried for 24 h in vacuum oven at 40^{o}C. The opaque white polymer was obtained.

3.5 Preperation of Blend of Fluorine Containing Homopolymer and Poly(*tert*-butyl acrylate)

In order to study the miscibility behavior of fluorine containing homopolymers, various binary blends of (1,1,1,3,3,3-hexafluoroisopropyl methacrylate), and (1H,1H,2H,2H-perfluorodecyl methacrylate) with poly(*tert*-butyl acrylate) were prepared in the weight ratios given in (Table 4.4) by dip coating from $CHCl_3$ solvent at room temperature. Then, the films were allowed to dry in a desicator overnight. Later surface properties of blend films were studied by contact angle measurements.

3.6 Characterization

Molecular weight and molecular weight distributions of polymers were measured by using a gel permeation chromatography (GPC) system consisting of an Agilent 1200 series pump, two Waters Styragel HR columns (5E, 3) and an Agilent 1100 RI detector, with a THF flow rate 0.3 ml min^{-1}. Poly(methyl methacrylate) standards from Poly Sciences Ltd. were used. Butyl lithium hydroxy toluene (BHT) was used as an internal standard. Measurements were done at Professor Metin H. ACAR's laboratory in I.T.U. FT-IR reflectance spectrum of polymers were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer with an Universal ATR attachment

with diamond and ZnSe tip. Measurements were recorded at Professor Sezai SARAC's laboratory in I.T.U.

The ^{1}H- NMR spectrum were recorded on a Varian AS 500 NMR Spectrometer (500 MHz) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Spectrums were recorded in Chemistry Department of Gebze Institue of Technology.

3.6.1 Film Formation by Dip Coating

Glass slides were coated by slow dipping (67 mm/min) at room temperature for 2 min. Before using glass slides, they were cleaned according to a special procedure. Glass slides which dimensions are 38mm x 26mm placed into a glass container having chromic acid solution (1 part of K_2CrO_4 and 4 part of H_2SO_4) for overnight at dark place. After acid shower glass slides were rinsed with water in order to eliminate acid traces and placed into DI water for two hours at least then the glass slides were dried in the oven at 100^{o}. Polymer solution were prepared in $CHCl_3$ having concentrations 20 mg/ml at room temperature. After dip coating, samples were dried at room temperature over night in a desicator.

The home-made mechanical dipper was located in Professor H.Yıldırım Erbil's laboratory, Chemical Engineering Department of Gebze Institue of Technology. It has an electric motor which a moving tweezer was connected going up and down with different speeds whose picture is given below.

Figure 3.4: Mechanical Dipper

3.6.2 Contact Angle Measurement

Water contact angle measurements were performed on polymer coated glass slides (38mm x 26 mm) using KSV Instruments, CAM 200, having digital camera which is capable of taking 30, 60, 100 frames per second, monochromatic light source which helps to assure a sharp image and drop dispenser. This instrument consists a special software get ready by KSV. The photograph of the instrument is given below.

Figure 3.5: Contact Angle Meter, KSV CAM 200

Equilibrium, advancing and receding contact angles were measured with the sessile drop method at room temperature on each coated glass slide. Three measurements were carried out on every sample and the mean value was reported as less than ± 1^{o}.

These angles fall within a range with advanced angles forming a maximum value and receded angles forming a minimum value.

Equilibrium contact angle was determined, when a 5 µl water droplet from the tip of the syringe was placed on the coated sample and the syringe was removed leaving the static droplet on the surface.

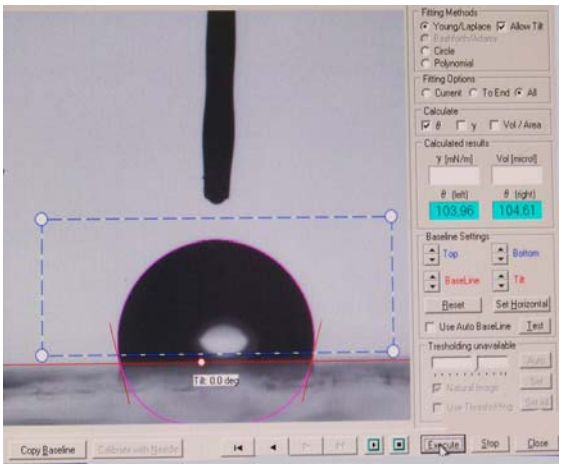


Figure 3.6: Equilibrium Contact Angle Measurement

Advancing contact angle was determined, when water droplet was expanding until having 5 ųl volume on the coated sample (the tip of the syringe was kept in the middle of the drop during measurement).

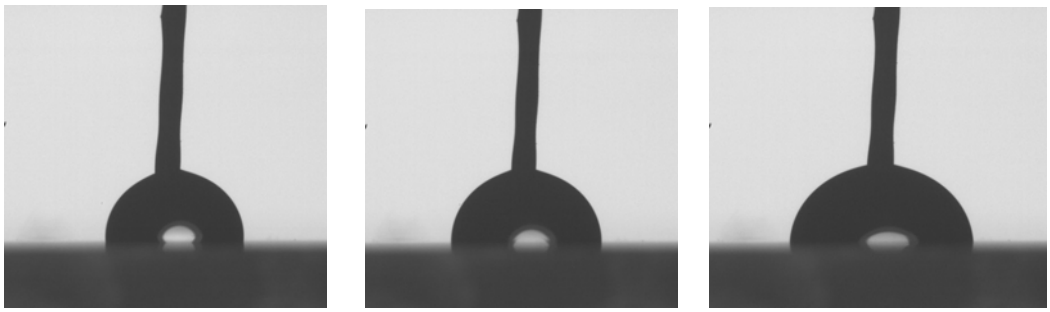


Figure 3.7: Advancing Contact Angle Measurement

Receding contact angle was also determined, when water initial 5 µl droplet was sucked by the automatic syringe system until having 3 µl liquid volume remain on the polymer surface (the tip of the syringe was kept in the middle of the drop during measurement).

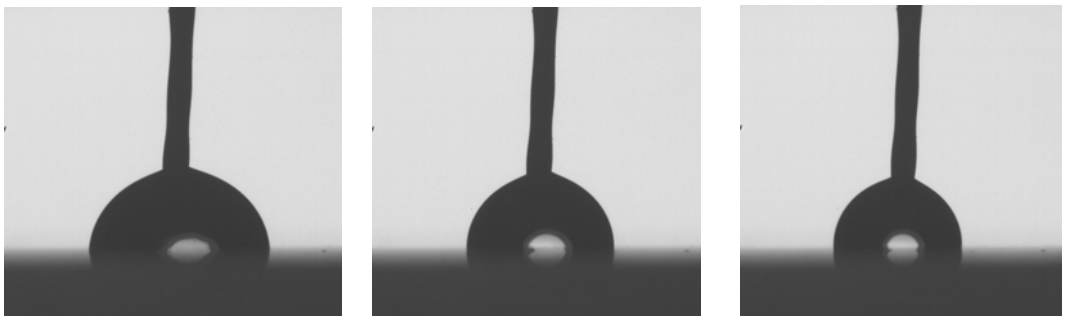


Figure 3.8: Receding Contact Angle Measurement

Two NIKON optic microscopes having digital cameras are also used to monitor the polymer surfaces with 1000X objectives.

4. RESULTS and DISCUSSION

4.1 Synthesis of P*t*BA, PFDMA, PHFMA, PTFMA, PMMA

Homopolymerizations of monomers were achieved via ATRP as described in experimental part. The polymerization conditions and results are given in Table 4.1. Number average of molecular weight (M_n) and polydispersity (PDI) of polymers were measured by GPC. Homopolymers were obtained in desired molecular weight with low polydispersity and generally, measured molecular weight of the polymer are found close to theoretical values. GPC traces of P*t*BA (Figure 4.1), PMMA and PTFMA show positive signal, whereas PFDMA, PHFMA (Figure 4.2) show negative signal because of the refractive index relative to the solvent [23].

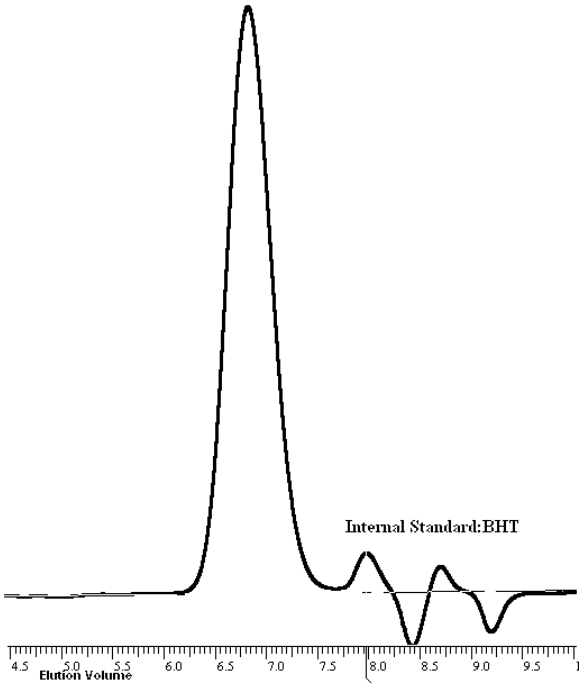


Figure 4.1: GPC of P*t*BA

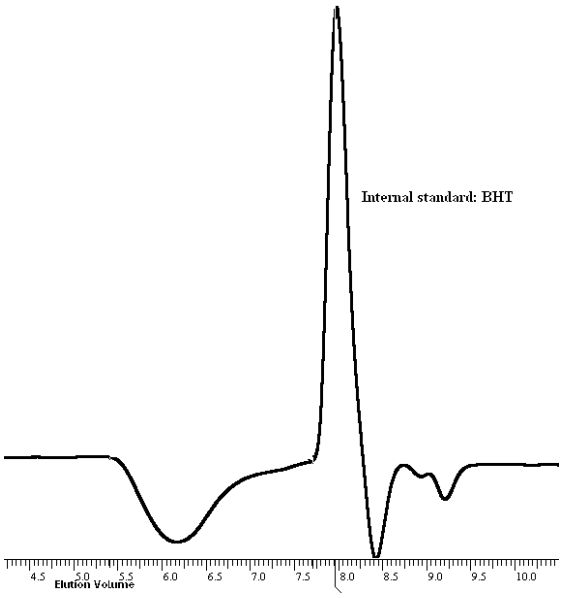


Figure 4.2: GPC of PHFMA

As representatively, FT-IR ATR spectrum of P*t*BA (run PP-1) is shown in Figure 4.3. In FT-IR spectra of P*t*BA, C=O:1900-1580 cm^{-1}; CH_3 and–CH_2:990-2850 cm^{-1}, C-O: 1280-1000 cm^{-1}; $C(CH_3)_3$: 1395 cm^{-1} (medium) and 1370 cm^{-1} (strong) were shown. In absence of vinyl (-C=CH_2) group peaks at 3080 cm^{-1} and 2995 cm^{-1} explain that the polymerization was achieved successfully.

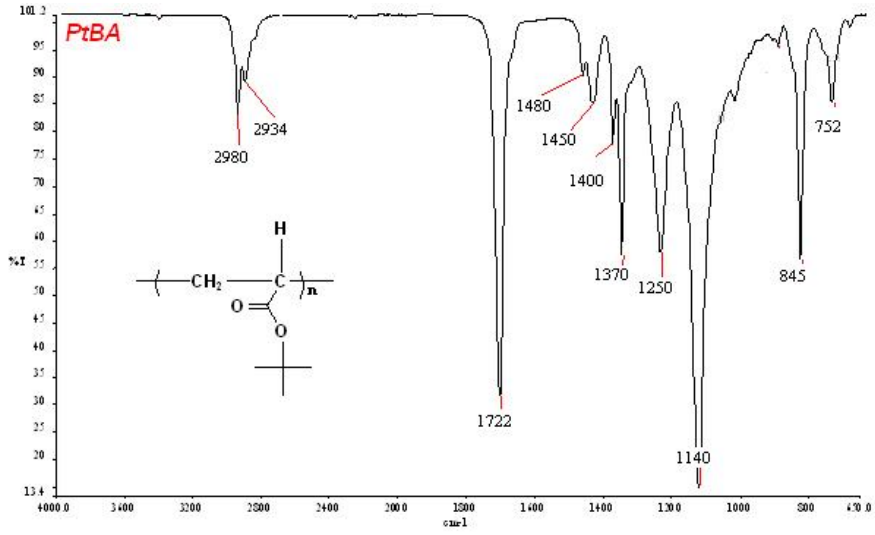


Figure 4.3: FT-IR spectrum of P*t*BA

Table 4.1: Homopolymers Synthesized via ATRP

Run (#)	Monomer	Solvent	$[M]_o$ ($mol.L^{-1}$)	$[M]_o/[I]_o$	Temp. (^oC)	Time (h)	Conv. (%)	M_{ntheo} [a]	M_{nGPC} [b]	PDI
PP-1 [c]	t-BA	Acetone 2 ml	5.2	25	60	2.5	89	2848	3500	1.14
PP-2[c]	t-BA	Acetone 12.5 ml	5.2	25	60	2.5	97	3100	2700	1.13
PP-3[d]	TFMA	Toluene 1 ml	4.8	50	80	48	48	4200	17000	1.39
HP-4[d]	PFDMA	Anisole 1 ml	2.0	15	80	20	71	5700	3900	1.06
HP-5 [e]	HFMA	Bulk	5.1	40	90	0.3	13	1230	11000	1.41

Run (#)	Monomer	Solvent	$[M]_o$ ($mol.L^{-1}$)	$[M]_o/[I]_o$	Temp. (^oC)	Time (h)	Conv. (%)	M_{ntheo}[a]	M_{nGPC}[b]	PDI
HP-6[d]	TFMA	Bulk	6.5	50	90	1	35	2940	11600	1.22
HP-7[d]	MMA	Toluene 5 ml	6.0	200	80	1.3	56	11200	22000	1.26
HP-8[d]	MMA	Toluene 20 ml	7.0	50	80	0.7	90	4500	4500	1.20
HP-9[d]	MMA	Toluene 5 ml	6.0	200	80	1.3	57	11400	18000	1.12

[a] $M_{n,theo} = ([M]_o/[I]_o)$x Conversion % x $(Mw)_o$

[b] Calculated from GPC calibrated with linear polymethyl methacrylate standards.

[c] $[I]_o:[CuBr]_o:[PMDETA]_o:[CuBr_2]_o$ = 1: 0.5: 0.5: 0.05, $[I]_o$: Methyl 2-Bromopropionate (MBrP).

[d] $[I]_o:[CuBr]_o:[PMDETA]_o$: = 1: 1: 1 , $[I]_o$: Ethyl 2-bromoisobutyrate (EBrB).

[e] $[I]_o:[CuBr]_o:[PMDETA]_o$: = 1: 1: 2

4.2 Synthesis of Block Copolymers

Block copolymers were carried out by ATRP as described in experimental part. ATRP mechanism of P*t*BA-*b*-PFDMA is shown as representatively in Figure 4.4. After some preliminary experiment, limited block copolymers were obtained due to low reactivity's of fluorinated monomer and solubility difficulties of fluorinated polymers.

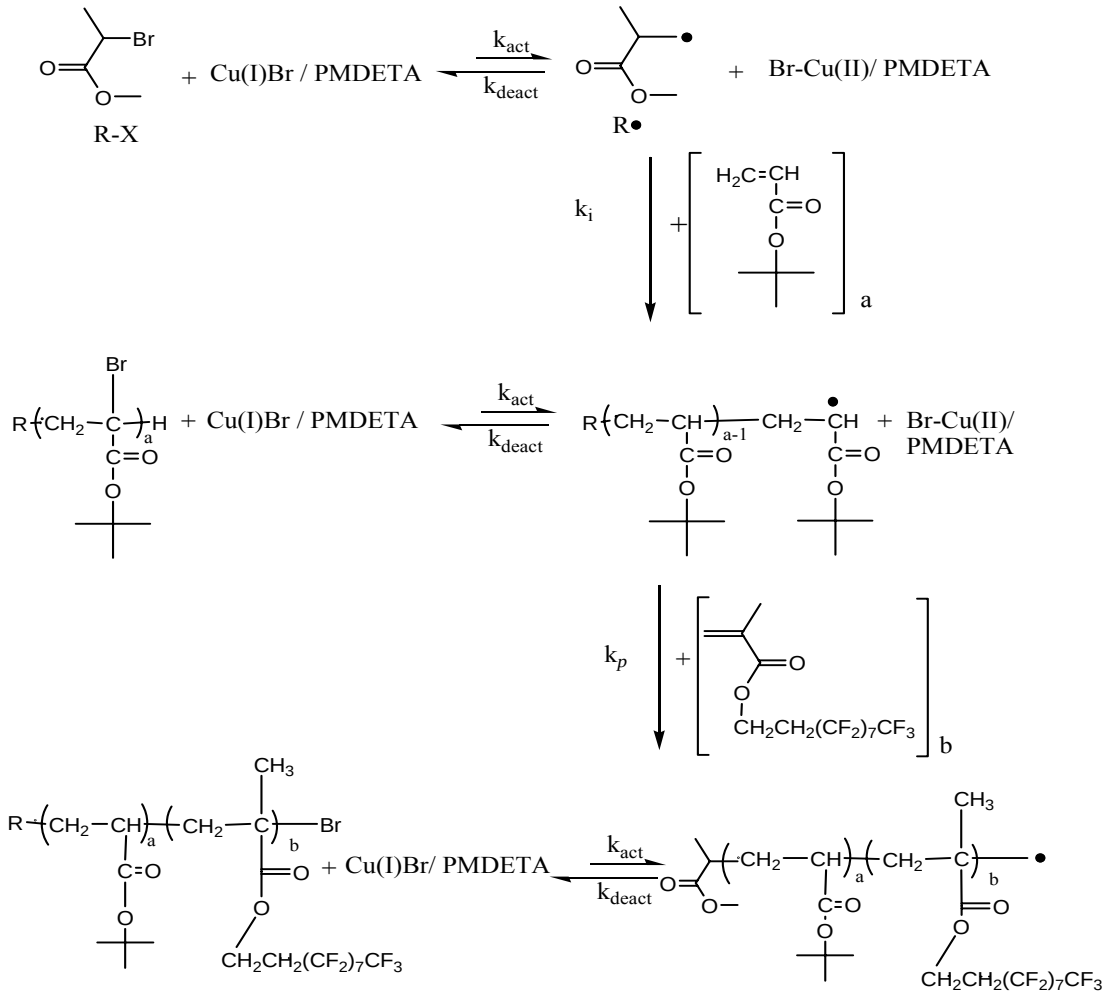


Figure 4.4: Atom Transfer Radical Polymerization of P*t*BA-*b*-PFDMA.

Whereas GPC traces of PHFMA, as can be seen in figure 4.2 is having the negative refractive index signal, GPC traces of P*t*BA-*b*-PHFMA (BCP-2) are shown positive signal while P*t*BA was using as macroinitiator (Figure 4.5). The changing signal polarity is also demonstrated that the block copolymerization were succeed.

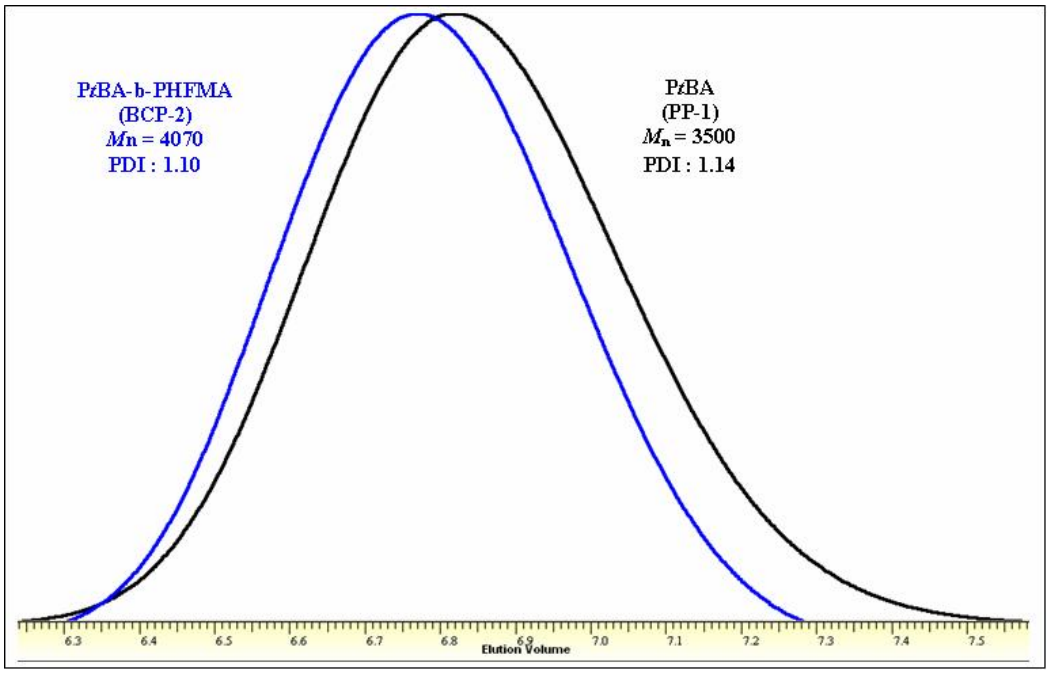


Figure 4.5: GPC of P*t*BA-*b*-PHFMA (BCP-2)

Overlay FT-IR spectra of P*t*BA (PP-1) and P*t*BA-*b*-PFDMA (BCP-3) are shown in Figure 4.6. Whereas FT-IR spectrum of P*t*BA (PP-1) are shown the signals for C=O: 1900-1580 cm^{-1}; CH_3 and–CH_2: 990-2850 cm^{-1}, C-O: 1280-1000 cm^{-1}; $C(CH_3)_3$: 1395 cm^{-1} (medium) and 1370 cm^{-1} (strong). In FT-IR spectrum of P*t*BA-*b*-PFDMA, C=O: 1900-1580 cm^{-1}; CH_3 and–CH_2:990-2850 cm^{-1}, C-O: 1280-1000 cm^{-1} $C(CH_3)_3$: 1395 cm^{-1} (weak) and 1370 cm^{-1} (weak) and additionally C-F: 1250-960 cm^{-1} (strong) and CF_2 :1150-1250 cm^{-1} signals are observed. The decreasing of signals intensities of *tert*-butyl group and existence of additional C-F and CF_2 signals indicates that second monomer was covalently bonded to the P*t*BA macroinitiator [68].

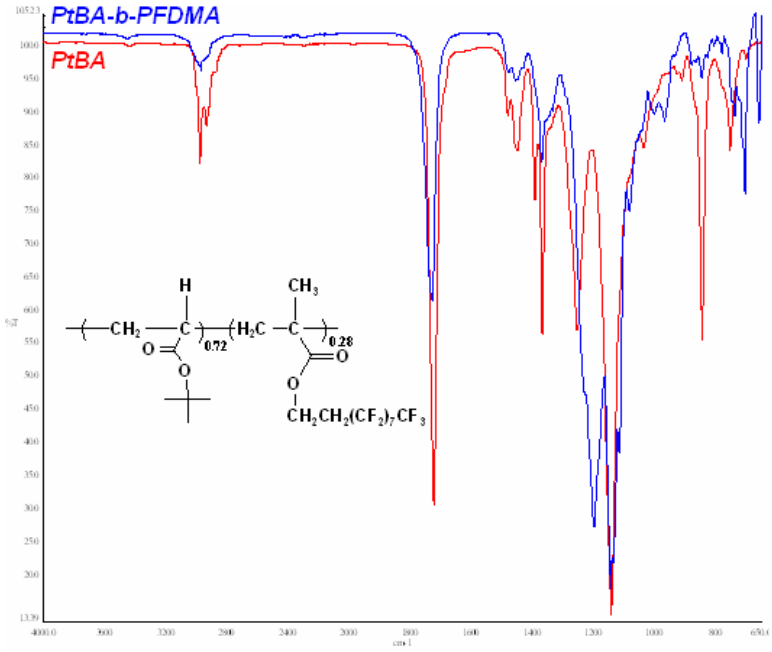


Figure 4.6: Overlay FT-IR Spectra of P*t*BA (PP-1) and P*t*BA-*b*-PFDMA (BCP-3)

The ^{1}H-NMR spectrum of compound P*t*BA-*b*-PTFMA (BCP-4) (Figure 4.7) shows that -C(CH_3)$_3$ protons at δ 1.46 ppm, and -CH- proton at δ 2.45 ppm belong to P*t*BA macroinitiator (PP-1); moreover, -CH_3 protons at δ 1.20-0.85 ppm and –CH_2 protons at δ 4.30 ppm belong to monomer 2,2,2-trifluoroethyl methacrylate, -CH_2 protons at δ 2-1.80 ppm belong to both two, those indicates the ATRP reaction was carried out successfully. Compositions of block copolymers were calculated from the ratio of the corresponding peak of the each monomer. 0.44/0.56 mol ratio was obtained for P*t*BA-*b*-PTFMA (BCP-4). The polymerization conditions and results are given in Table 4.2.

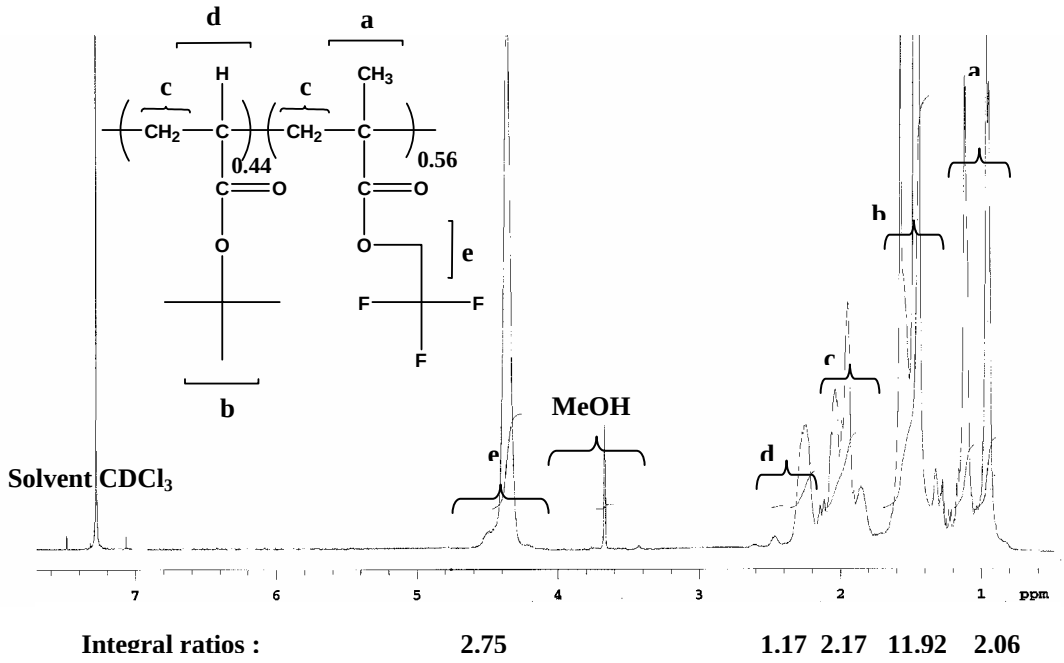


Figure 4.7: The ^{1}H-NMR Spectrum of BCP-4 (P*t*BA-*b*-PTFMA) in $CDCl_3$

As can be seen from Table 4.2, block copolymer containing fluorinated monomer were synthesized by low polydispersity. In order to reach high yield long polymerization time is required. While tBA chose TAN instead of TM when it was polymerized. MMA was not polymerized with neither TAN nor TM.

Table 4.2: Block Copolymers Synthesized via ATRP

Run (#)	Macroinitiator (10^{-4} mol)	Monomer	$[M]_o/[I]_o$	Solvent	Temp (^oC)	Time (h)	%Conv.[a]	mol % of fluorinated segments[b]	M_{nGPC}[c]	PDI
BCP-1[d]	PP-1 (2.9)	PFDMA	10	Toluene	100	72	17	5	4900	1.10
BCP-2[e]	PP-1 (1.4)	HFMA	35	$CHCl_3$	90	4	7	34	4100	1.10
BCP-3[e]	PP-1 (1.1)	PFDMA	10.5	Anisole	100	144	78	28	8700	1.18
BCP-4[e]	PP-1 (2.9)	TFMA	22	Toluene	100	48	75	56	7000	1.07
BCP-5[e]	PP-2 (7.4)	TFMA	27	$CHCl_3$	90	4	32	65	3100	1.16
BCP-6[f]	PP-3 (0.6)	MMA	170	$CHCl_3$	90	10	70	64	30000	1.06
BCP-7[d]	PP-2 (3.7)	TAN	10	Toluene	100	312	41	-	7700	1.10
BCP-8[d]	PP-2 (3.7)	TM	10	Toluene	100	312	-	-	h	-
BCP-9[g]	HP-9 (0.55)	TAN	32	Toluene	100	264	-	-	h	-

Run (#)	Macroinitiator (10^{-4} mol)	Monomer	$[M]_o/[I]_o$	Solvent	Temp (^oC)	Time (h)	%Conv.[a]	mol % of fluorinated segments[b]	M_{nGPC}[c]	PDI
BCP-10[g]	HP-9 (0.55)	TM	34	Toluene	100	264	-	-	h	-
BCP-11[e]	PP-2 (10.7)	TFMA	9	Toluene	100	144	66	-	4500	1.42
BCP-12[d]	HP-9 (10.7)	TFMA	109	Toluene	100	144	26	-	22800	1.28

[a] Conversions were calculated by gravimetric measurements

[b] Calculated from ^{1}H-NMR

[c] Calculated from GPC calibrated with polymethyl methacrylate standards

[d] $[I]_o : [CuBr]_o : [PMDETA]_o = 1 : 1 : 2$

[e] $[I]_o : [CuBr]_o : [PMDETA]_o = 1 : 1 : 1$

[f] $[I]_o : [CuBr]_o : [PMDETA]_o = 1 : 1.75 : 3.5$

[g] $[I]_o : [CuBr]_o : [PMDETA]_o = 1 : 2 : 4$

[h] Same value with its macroinitiator

4.3 Copolymerization of MMA and Fluoroalkyl (Meth)acrylate by Free Radical Polymerization

Copolymerizations of monomers were prepared by free radical polymerization methods either in $scCO_2$ or in solution. The polymerization conditions and results were given in Table 4.3.

The representative ^{1}H-NMR spectrum of compound PMMA-*co*-TAN (CP-10) (Figure 4.8) showed that the -O-CH_3 protons at δ 3.60 ppm and -CH_3 protons at δ 1.50-0.70 ppm belong to methyl methacrylate. Moreover, -OCH_2- protons at δ 4.40-4.10 ppm and –CH_2-protons at δ 2.50 ppm belong to Zonyl TAN so indicates the free radical polymerization was carried out successfully. Compositions of random copolymers were calculated from the ratio of the corresponding peak of the each monomer. 0.94/0.06 mol ratio was obtained for PMMA-*co*-TAN (CP-10).

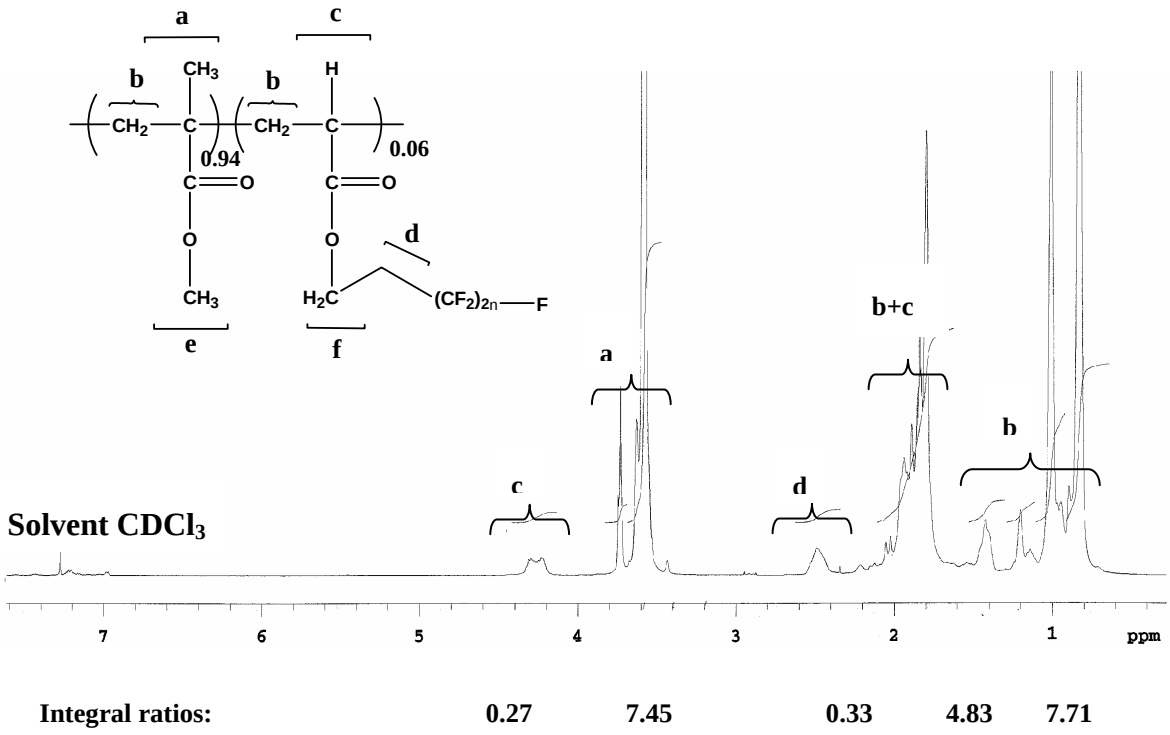


Figure 4.8: The ^{1}H-NMR spectrum of PMMA-*co*-TAN (CP-10) in $CDCl_3$

Table 4.3: Copolymers Synthesized via Free Radical Polymerization

Run (#)	MMA (mol)	Monomer-2	A	B	C	D	$M_{n,GPC}$ [a]	PDI
CP-1 [b]	0.1	TAN	2	4	0.35	0.80	8800	1.4
CP-2 [b]	0.1	TAN	7	10	1.28	2.00	6200	3.7
CP-3 [b]	0.1	TAN	5	5	0.90	1.00	6400	1.6
CP-4 [b]	0.1	TAN	9	11	1.70	2.00	16000	1.7
CP-5 [b]	0.07	TAN	30	27	7.00	6.00	7000	1.7
CP-6 [b]	0.05	TAN	23	15	5.00	3.00	9500	3.0
CP-7 [b]	0.05	TM	23	32	5.00	8.00	6700	2.9
CP-8 [b]	0.07	TM	30	37	7.40	10.00	6300	3.3
CP-9 [c]	0.1	TAN	5	11	0.90	2.00	50000	2.0
CP-10 [d]	0.1	TAN	17	27	3.40	6.00	26000	1.5
CP-11 [e]	0.1	TAN	23	38	5.00	10.00	22000	1.5
CP-12 [e]	0.1	TM	23	37	5.00	10.00	19000	2.2

[a] Calculated from GPC calibrated with polymethyl methacrylate standards

[b] $[M]_o/[I]_o = 50$; 4 hours at 80 ^oC, in $scCO_2$ solvent under 200 bar (2900 psi)

[c] $[M]_o/[I]_o = 80$; 2 hours at 95 ^oC in bulk under 1 atm

[d] $[M]_o/[I]_o = 50$; 2 hours at 95 ^oC in 10 ml toluene under 1 atm

[e] $[M]_o/[I]_o = 50$; 2 hours at 95 ^oC in 5 ml toluene under 1 atm

Table 4.3 belongs to copolymers synthesized via free radical polymerization, capital letters A, B, C, D indicate weight% monomer-2 (Feed), weight% monomer-2 (NMR), mol% monomer-2 (Feed), mol% monomer-2 (NMR) respectively

4.4 Contact Angle Measurements of Polymer Coated Samples

Table 4.4 and Figure 4.9 shows the advancing contact angle values increases with increasing PHFMA weight content for Blend of P*t*BA and PHFMA up to 49 % (w/w) PHFMA content which is same as in % weight result from ^{1}H-NMR of P*t*BA-*b*-PHFMA.

Table 4.4: The Contact Angle Values of Blend of P*t*BA and PHFMA

Run # (P*t*BA, 0.6 g)	Addition PHFMA (g)	Contact Angles		
		Equilibrium	Advancing	Receding
0	-	69	78	71
1	0.003	96	106	93
2	0.006	108	110	101
3	0.012	109	111	101
4	0.300	111	113	109
5	0.060	110	113	99
6	0.039	108	115	96
7	0.050	100	115	90
8	0.057	95	116	88
9	0.052	96	115	85
10	0.060	97	115	88
11	0.090	97	114	87
12	0.110	95	114	86

The advancing contact angle value indicates 114^{o} with red point on the plot. The advancing contact angle value of blend or block was not higher than the homopolymer PHFMA's contact angle value of 118^{o}.

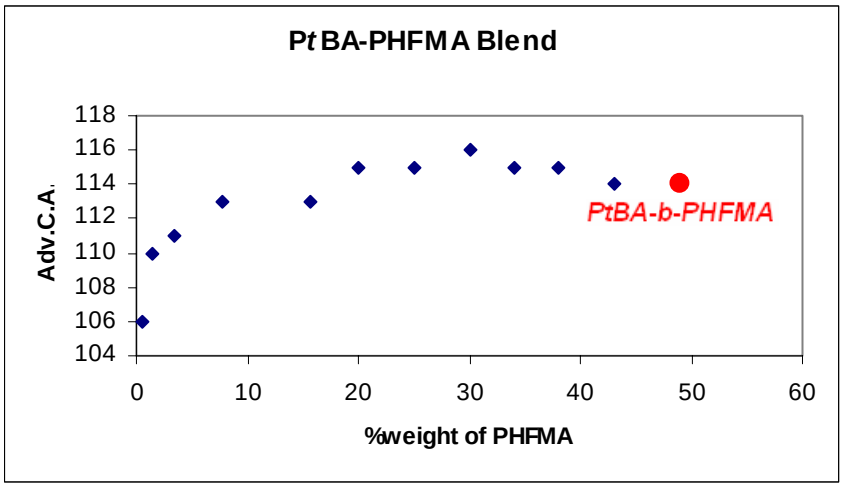


Figure 4.9: Plot of Contact Angle Measurement of P*t*BA and PHFMA Blend

The incorporation of PHFMA homopolymer into the blend increases the contact angle of the blend from PtBA contact angle value ,78^{o} to 113^{o} when PHFMA was added less than 10 % by weight.

Also, we prepared a blend containing P*t*BA and 18% (w/w) PFDMA of it, the advancing contact angle was not shown over than 124^{o} indicating as in % weight result from ^{1}H-NMR of P*t*BA-*b*-PFDMA .(Table 4.5 and Table 4.6)

Table 4.5: The Contact Angle Measurements of Blend Homopolymers of P*t*BA and PFDMA

P*t*BA	Addition of PFDMA	Contact Angles		
		Equilibrium	Advancing	Receding
0.6 g	0.108 g	119	124	102

Table 4.6: Advancing Contact Angle of Block Copolymers

Run #	Block Copolymers	Adv.C.A.	Fluorinated Segment	
			%Weight[a]	%Mol[a]
BCP-1	P*t*BA-*b*-PFDMA	126	18	5
BCP-2	P*t*BA-*b*-PHFMA	114	49	34
BCP-3	P*t*BA-*b*-PFDMA	N/A	62	28
BCP-4	P*t*BA-*b*-PTFMA	111	63	56
BCP-5	P*t*BA-*b*-PTFMA	113	70	65
BCP-6	PTFMA-*b*-PMMA	104	76	64

[a] Calculated from ^{1}H-NMR

If we examine the advancing contact angle measurements of block copolymers, P*t*BA-*b*-PFDMA shows highest value among the other blocks because PFDMA have maximum fluorine contents. Its contact angle was not over than 128^{o} which is PFDMA homopolymer. Table 4.6 shows the advancing contact angle increases with increasing fluorine contents but it is no higher than their fluorine containing homopolymer's advancing contact angle. These are 114^{o}, 118^{o} and 128^{o} for PTFMA, PHFMA and PFDMA respectively. Also water contact angles of P*t*BA and PMMA are measured as 78^{o} and 80^{o}, respectively. Fluoroalkyl (meth)acrylates which are TAN and TM have almost same advancing contact angle; 125^{o}and 128^{o} respectively.

Table 4.6 shows, it is possible to obtain a high advancing contact angle value even if block copolymer is synthesized consisting 18% weight of fluorine derivatives. This goal was obtained by using a high number of fluorine atom containing monomer.

Although we obtained almost same contact angle values from samples, these polymers could be used for different applications. For example, block copolymers covalently bonded are used as amphiphilic surfactant to form micelles. These can be

used as coating material to get low surface energy surfaces, however these are not seperated with any effect. Blend of fluorinated homopolymers also can be used for this purpose but these are seperated from each other with any solvent effect.

Table 4.7 indicates a quite difference between copolymers consist of TAN and TM monomers. Fluorine composition of TAN is higher than TM monomer. This difference may cause a sensible difference in contact angles. Another approach is that, there is a further properties coming from behavior of monomers in $CHCl_3$ solvent.

Table 4.7: Contact Angle (CA) and Film Thickness (FT) of Copolymers Synthesized via Free Radical Polymerization

Run (#)	Fluorinated Monomer		Dipping rate					
			816 mm/min		612 mm/min		336 mm/min	
	w%	mol%	Adv.CA	FT, μm	Adv.CA	FT, μm	Adv.CA	FT, μm
CP-1	TAN		95	0.81	90	0.61	93	0.40
	4	0.8						
CP-2	TAN		110	0.56	104	0.35	104	0.25
	10	2						
CP-3	TAN		104	0.76	102	0.66	100	0.51
	5	1						
CP-4	TAN		125	0.51	117	0.81	116	0.15
	11	2						
CP-5	TAN		121	0.76	121	0.58	122	0.40
	27	6						

Run (#)	Fluorinated Monomer		Dipping rate					
			816 mm/min		612 mm/min		336 mm/min	
	w%	mol%	Adv.CA	FT, μm	Adv.CA	FT, μm	Adv.CA	FT, μm
CP-6	TAN 15	3	124	1.06	123	1.06	122	0.76
CP-7	TM 32	8	113	0.30	114	0.18	114	0.13
CP-8	TM 37	10	115	0.38	117	0.25	116	0.15
CP-9	TAN 11	2	114	0.20	109	0.23	110	0.23
CP-10	TAN 27	6	120	0.96	121	0.89	122	0.73
CP-11	TAN 38	10	124	1.09	122	1.06	124	0.68
CP-12	TM 37	10	114	0.89	116	0.78	116	0.56

If we examine three plots in table 4.7 and figure 4.10, it was obtained an evidence about fluorine composition in which consist in copolymers via free radical polymerization. According to this study, it is possible to obtain a high advancing contact angle value even if copolymer is synthesized consisting 15% weight of fluorine derivatives in $scCO_2$ medium. Another point of view, if copolymer is synthesized consisting 27-37% weight of fluorine derivatives in solution polimerization. This goal was obtained by using a high number of fluorine atom containing monomer. This study was shown that if we want to obtain high advancing contact angle value, it should be synthesized copolymer with minimum fluorine containing monomer in $scCO_2$ medium.

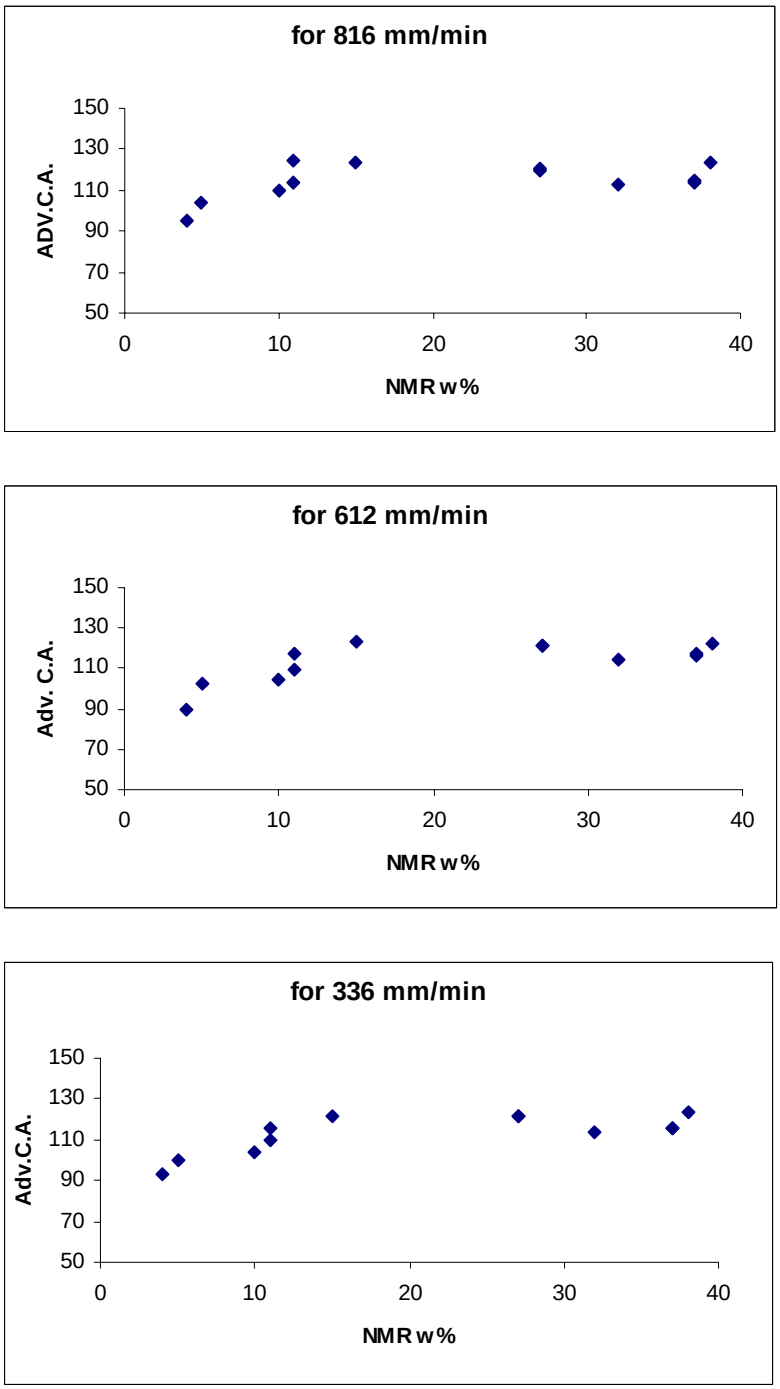


Figure 4.10: Relationship Between Fluorinated Monomer Content in NMR w% and Advancing Contact Angle for Different Speed of Dip Coating

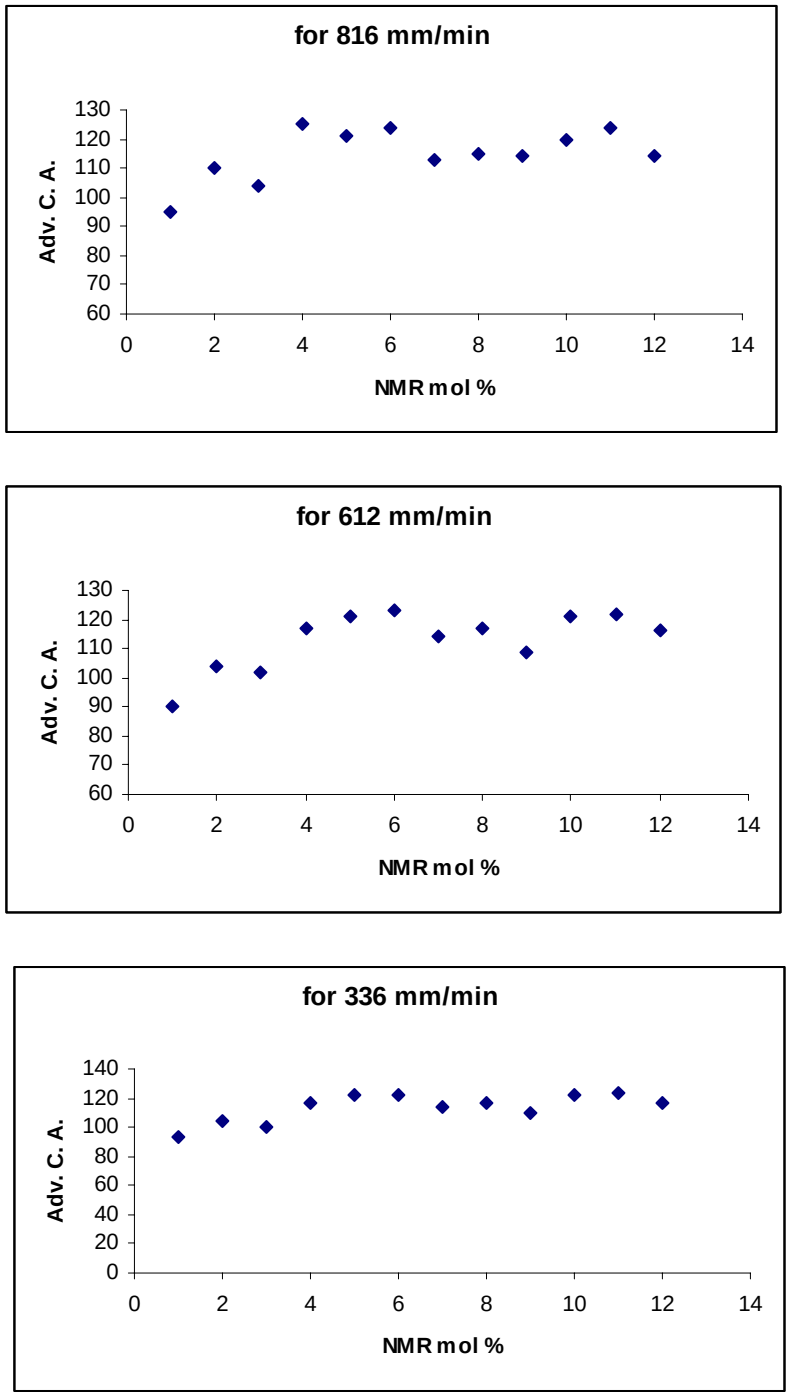


Figure 4.11: Relationship Between Fluorinated Monomer Content in NMR mol% and Advancing Contact Angle for Different Speed of Dip Coating

If we examine three plots in figure 4.12, contact angles are not effected by film thickness if the dip coating speed is changed

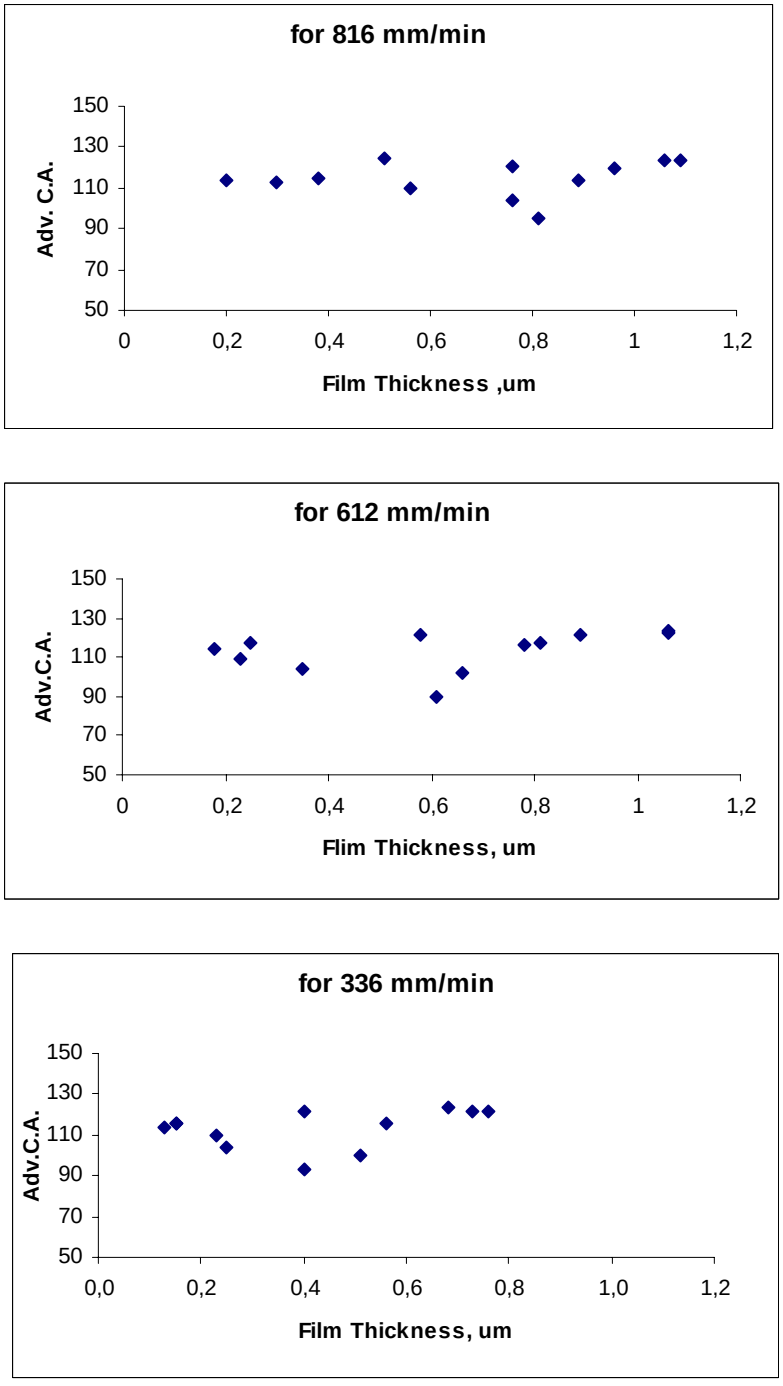


Figure 4.12: Relationship Between Film Thickness and Advancing Contact Angle for Different Dip Speed of Coating

As it was seen from Table 4.2, some block copolymer could not be synthesized via ATRP method, such as P*t*BA-TM, PMMA-TAN and PMMA-TM. Although experiment was taken long time, non of monomers could not be polymerized. When the reactions were carrying out for other monomers, precipitation was observed in toluene medium. This means that reaction was not under the control, due to solubility problem of fluorinated monomers. In this study, three reaction conditions were applied in order to obtain fluorinated polymers.

One of this was ATRP, the others were free radical polymerizations in solution and in $scCO_2$ medium.

One of the problem in ATRP, is removal of the catalyst. The metal catalyst–ligand complex is undesired in the product, as the transition metal induces aging in the polymer, but also coloration therefore catalyst removal is important. Catalyst removal is difficult and costly. One of purification method includes running the raw product on an alumina columns and precipitation of polymer which is a successful method to obtain polymers with desired molecular weight.

Dispersion polymerization is a heterogeneous reaction process in $scCO_2$ medium. It begins with the formation of a homogeneous mixture due to the solubility of both the monomer and the initiator in the continuous phase when using a suitable stabilizer. Polymerization takes place initially through a solution phase reaction to produce oligomeric radicals. When the growing oligomeric radicals reach a critical chain length, the chains become insoluble in the continuous phase and precipitate in the $scCO_2$ medium. To achieve a successful dispersion polymerization, and to prevent flocculation of particles in $scCO_2$, a surface active stabilizing molecule must be used. Its role is to physically adsorb or chemically attach to the surface of the polymeric particles and form stable nuclei. The effectiveness of a stabilizer is governed by two factors; firstly there must be sufficiently strong anchoring to the polymer particle, and secondly the soluble segment must be chain extended into the continuous phase thus facilitating a negative steric interaction between particles (e.g. of sufficient solvation and chain length). These factors can be controlled by synthetic variation of both the composition and architecture of the stabilizers for the polymerization reactions in $scCO_2$ medium. Stabilizers can be classified as either CO_2-philic or CO_2-phobic based on their solubility characteristics. In order to perform dispersion

polymerizations, amorphous fluoropolymers and polysiloxanes are used because of their solubility in $scCO_2$, while most other polymers are insoluble in $scCO_2$.

Polymers obtained from $scCO_2$ experiments had number average molecular weight lower than 10.000 g mol^{-1}, except CP-4. This means that polymers start to precipitate after reach to certain chain length under 200 bar. However, there was no problem with removal of unreacted monomers and coloration compared to ATRP.

Polymers were also obtained from solution polymerization had number average molecular weight higher than 10.000 g mol^{-1} with high conversion, but uncontrolled.

5. CONCLUSION

In this study fluorine containing copolymers having different fluorine composition, via atom transfer radical polymerization (controlled / "living" radical polymerization) and free radical polymerization was carried out in solution or super critical carbon dioxide medium was prepared. Polymers were obtained via ATRP in desired molecular weight with low polydispersity and generally, measured molecular weight of the polymer are found close to theoretical values, however it was faced many solubility problems about fluorinated polymers in commercial solvents as reported in Table A.1.

Characterization of surface properties, the contact angle measurement was used. By doing this, we may able to examine the changes contact angles of water on polymer surfaces with differences of fluorine composition and copolymer types. Contact angle of block copolymer and blend of homopolymer were shown almost similar values. (Table 4.4-4.5) Block copolymers containing covalently bonded two segments can be used as amphiphilic surfactant to form micelles. These can be used as coating material to get surfaces with low free energy. On the other hand, blend of fluorinated homopolymers also can be used for this purpose but two segments could be seperated from each other with any solvent.

It is easy to obtain advancing contact angle value higher than 100^{o} when copolymer are containing at least 10% weight of fluorinated monomers which can be synthesized in solution or scCO_2 medium. This goal was obtained by using a blend of non-fluorinated homopolymer and fluorinated homopolymer. In case of fluorinated block copolymer was examined, high contact angle value was obtained when fluorinated monomer was used higher than 20% weight.

REFERENCES:

[1] **Hamley, I. W.,** 2004. Developments in Block Copolymer Science and Technology, John Wiley & Sons

[2] **Cai-Yuan, P. and Chun-Yan, H.,** 2004. Developments in Block Copolymer Science and Technology, John Wiley & Sons

[3] **Jankova, K. and Hvilsted, S.,** 2005. Novel fluorinated block copolymer architectures fuelled by atom transfer radical polymerization, *Journal of Fluorine Chemistry*, **126**, 241-250

[4] **Zhang. Z. B., Ying. S. K. and Shi. Z. Q.,** 1999. Synthesis of fluorine-containing block copolymers via ATRP 2. Synthesis and characterization of semifluorinated di- and triblock copolymers, *Polymer*, **40**, 5439-5444

[5] **Matyaszewski, K.,** 2006. Controlled/living radical polymerizations: from synthesis to materials, ACS, Oxford University Press

[6] **Taek Lim. K., Young Lee. M., Jun Moon. M., Dae Lee. G., Hong. S., Dickson. J.L. and Johnston. K.P.,** 2002. Synthesis and properties of semifluorinated block copolymers containing poly(ethylene oxide) and poly(fluorooctyl methacrylates)via atom transfer radical polymerization, *Polymer,* **43,** 7043-7049

[7] **Tanko. J. M.,** 2003. Free-Radical Chemistry in Supercritical Carbon Dioxide; Green chemistry using liquid and supercritical carbondioxide edited by DeSimone. J. M., & Tumas. W., Oxford University Press

[8] **Darling, TR., Davis, TP., Fryd, M., Gridnev, AA., Haddleton, DM. and Ittel, SD.,** et al. 2000. Living polymerization: rationale for uniform terminology, *J. Polym Sci, Part A: Polym Chem,* **38**(10), 1706

[9] **Natanya. M.L. Hansen, Jankova. K. and Hvilsted. S.,** 2007. Fluoropolymer materials and architectures prepared by controlled radical polymerizations, *E. Polym. J.,* **43,** 255-293

[10] **Nishino, T., Urushihara, Y., Meguro, M. and Nakamae, K.,** 2005. Surface properties and structure of diblock copolymer and homopolymer with perfluoroalkyl side chains, *J. Coll. Int. Sci.,* **283**, 533-538

[11] **Imae, T., Tabuchi, H., Funayama, K., Sato, A., Nakamura, T. and Amaya, N**., 2000. Self-assemblies of block copolymer of 2-perfluorooctylethyl methacrylate and methyl methacylate, *Coll. Surf. A: Phys.chem. Eng. Asp*.**167**, 73-81

[12] **Tang, L., Li, Y., Wu, X., Shan, X. and Wang, W.,** 2004. Synthesis and properties of fluoroacrylate coatings, *Polym. Adv. Tech*., **15**, 39-42

[13] **Saidi, S., Guittard, F., Guimon, C. and Geribaldi, S.**, 2005. Fluorinated acrylic polymers: surface properties and XPS ınvestigations, *J. Ap. Poly. Sci*., **99**, 821-827

[14] **Saidi, S., Guittard, F., Guimon, C. and Geribaldi, S.**, 2006. Synthesis and characterization of copolymers based on Styrene and partially fluorinated acrylates, *E. Poly. J.*, **42**, 702-710

[15] **Imae, T.,** 2003. Fluorinated Polymers, *Cur.Op. Col. and Int. Sci***. 8,** 307-314

[16] **Krupers, M. J. and Möller, M**., 1997. Semifluorinated diblock copolymers. Synthesis, characterization and amphiphilic properties., *Macromol. Chem. Phys*., **198**, 2163-2179

[17] **Hillmyer, M.A. and Lodge, T.P**., 2002. Synthesis and self-assembly of fluorinated block copolymers, *J. Polym. Sci. Part A:Polym Chem*., **40**, 1-8

[18] **Matsumoto, K., Kubota, M., Matsuoka, H. and Yamaoka**, **H.,** 1999. Water-soluble fluorine containing amphiphilic block copolymer: synthesis and aggregation behavior in aqueous solution, *Macromolecules,* **32**, 7122-7127

[19] **Zhang, Z.B., Ying, S.K., Hu, Q.H., Xu, X.D.**, 2001. Semifluorinated ABA triblock copolymers: synthesis, characterization, and amphiphilic properties, *J. Appl. Polym. Sci*., **83**, 2625-2633

[20] **Li, K., Wu, P. and Han, Z.,** 2002. Preparation and surface properties of fluorine-containing diblock copolymers, *Polymer*, **43**, 4079-4086

[21] **Pittman AG.** In:Wall LA, editor.1972. Fluoropolymers, vol.25. p.419, New York:Wiley

[22] **Acar, M.H. and Yağcı, Y.,** 1991. Studies on the block copolymerization of methacrylonitrile and hexafluorobutylmethacrylate using phenylazotriphenylmethane as thermal iniferter, *Macromolecular Reports*, **A28**, 177-183

[23] **İnceoglu, S., Solar, C. O., Acar, M.H. and Mayes, A.M.,** 2004. Atom transfer radical polymerization using poly(vinylidene fluoride) as macroinitiator, *Design. Monom. and Polym.*, **7**, 181-189

[24] **Liu, Y., Wang, L. and Pan, C.Y**., 1999. *Macromolecul*es, **32**, pp. 8301

[25] **Hawker, C.J., Bosman, A.W. and Harth, E**., 2001. *Chem.Rev*., **101**, pp.3661

[26] **Matyjaszewski, K. and Xia, J**., 2001. Atom Transfer Radical Polymerization, ACS, *Chem. Rev*, **101**, 2921–2990.

[27] **Acar M. H. and Bicak N**., 2003. Synthesis of hexylated triethylenetetramine: New ligand for homogeneous Atom Transfer Radical Polymerization, *Journal of Polymer Science Part A-Polymer Chemistry*, **41**, 1677-1680.

[28] **Xia, J., Zhang, X. and Matyjaszewski, K**., 2000. In Transition Metal Macromolecular Design; Boffa, L. S.; Novak, B. M., Eds.; *ACS Symposium Series* 760; American Chemical Society: Washington, DC., pp 207–223.

[29] **Allcock, H. R. and Lampe, F. W**. 1990, Contemporary Polymer Chemistry. 2nd. Ed., Prentice Hall: New Jersey

[30] **Matyjaszewski, K.,** 1994. From living carbocationic to living radical polymerization, *J. Macromol. Sci., Pure Appl. Chem.*, **A31**, 989.

[31] **Matyjaszewski, K., and Sigwalt, P**., 1994. Unified approach to living and nonliving cationic polymerization of Alkenes, *Polymer Int.,* **35**, 1.

[32] **Kato, M., Kamigaito, M., Sawamoto, M., and Higashimura, T**., 1995. Living cationic and radical polymerizations via reversible activation of carbon halogen bonds, *Abstracts of paper of the ACS* **209**:180-Poly. Part 2

[33] **Wang, J. S. and Matyjaszewski, K.,** 1995. Controlled living radical polymerization-halogen atom transfer radical polymerization promoted by a Cu(I)/Cu(II) redox process, *Macromolecules*, **28**, 7901–7910.

[34]**Wang, J. S. and Matyjaszewski, K**., 1995. Controlled living radical polymerization-ATRP in the presence of transition-metal complexes, *J. of Am. Chem Soc*, **117(20),** 5614–5615.

[35] **Matyjaszewski, K.,** 1998. Ed. Controlled Radical Polymerization*; ACS Symposium Series* No. **685**; American Chemical Society: Washington, DC,

[36] **Matyjaszewski, K.,** 2000. Ed. Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT; *ACS Symposium Series* No. **768**; American Chemical Society: Washington, DC.

[37] **Patten, T. E. and Matyjaszewski, K**., 1998. ATRP and the synthesis of polymeric materials. *Adv. Mater*., **10**, 901.

[38] **Matyjaszewski, K.,** 1999. Transition metal analysis in controlled radical polymerization:ATRP, *Chem. Eur. J.*, **5**, 3095.

[39] **Patten, T. E. andMatyjaszewski, K**., 1999. Copper(I) catalyzed ATRP, *Acc Chem Res*, **32 (10),** 895–903.

[40] **Kamigaito, M., Ando, T. andSawamoto, M.**, 2001. Metal-catalyzed living radical polymerization, *Chem Rev*, **101**, 3689–3746.

[41] **Matyjaszewski, K. and Xia, J.,** 2002. In Handbook of Radical Polymerization; Matyjaszewski, K., Davis, T. P., Eds., Wiley: New York

[42] **Davis, K.A. and Matyjaszewski, K**., 2000. ATRP of tert-butyl acrylate and preparation of block copolymers, *Macromolecules*, **33**, 4039.

[43] **Xia, J. and Matyjaszewski, K.,** 1997. Controlled/living radical polymerization. Homogeneous reverse ATRP, *Macromolecules*, **30**, 7697–7700.

[44] **Xia, J. H. and Matyjaszewski, K.,** 1997. Controlled/living radical polymerization. ATRP using multidentate amine ligands, *Macromolecules*, **30**, 7692–7696.

[45] **Wang, J. L., Grimaud, T. And Matyjaszewski, K**., 1997. Kinetic study of the homogeneous ATRP of methyl methacrylate, *Macromolecules*, **30**, 6507– 6512.

[46] **Matyjaszewski, K. and Davis, K.A.,** 2001. ABC triblock copolymers prepared using ATRP techniques, *Macromolecules*, **34 (7)** ,2101-2107.

[47] **Xia, J. and Matyjaszewski, K.,** 1999. Homogeneous reverse ATRP of Styrene initiated by peoxides, *Macromolecules*, **32**, 2434–2437.

[48] **Xia, J., Gaynor, S. G. and Matyjaszewski, K.,** 1998. Controlled/living radical polymerization. ATRP of acrylates at ambient temperature, *Macromolecules*, **31**, 5958–5959.

[49] **Shipp, D. A. and Matyjaszewski, K**., 2000. Kinetic analysis of controlled/living radical polymerzation by simulations, *Macromolecules*, **33,** 1553.

[50] **Matyjaszewski, K.,** 1999. New (co)polymers by ATRP, *Macromolecular symposia*, **143**: 257-268

[51] **Matyjaszewski, K. and Miller, P.J.,** 1999. ATRP of (meth)acrylates from dimethylsiloxane macroinitiators, *Macromolecules*, **32(26),** 8760-8767

[52] **Yoon, S.C. and Ratner, B.D.,** 1986. Surface structure of segmented poly(ether urethanes) and poly(ether urethane ureas) with various perfluoro chain extenders, *Macromolecules*, **19**, 1068-1079

[53] **Yoon, S.C. and Ratner, B.D.,** 1988. Surface and bulk structure of segmented poly(ether urethanes) with various perfluoro chain extenders 2, *Macromolecules*, **21**, 2392-2400

[54] **Yoon, S.C. and Ratner, B.D.,** 1988. Surface and bulk structure of segmented poly(ether urethanes) with various perfluoro chain extenders 3, *Macromolecules*, **21**, 2401-2404

[55] **McLain, S.J., Sauer, B.B. and Firment, L.E.,** 1996. Surface properties and metathesis synthesis of block copolymers including perfluoroalkyl-ended polyethylenes, *Macromolecules*, **29**, 8211-8219

[56] **Xu, B., Li, L., Yekta, A., Masoumi, Z., Kanagalingam, S. and Winnik, M.A**., et al. 1997. Synthesis, characterization, and rheological behavior of polyethylene glycols end-capped with fluorocarbon hydophobes, *Langmuir*, **13**, 2447-2456

[57] **Loppinet, B. and Gebel, G**., 1998. Rodlike colloidal structure of short pendant chain perfluorinated ionomer solutions, *Langmuir*, **14**, 1977-1983

[58] **Tadano, K., Tanaka, Y., Shimizu, T. and Yano, S**., 1999. Dielectric relaxation studies on molecular motion of poly(fluoroalkyl α-substitued acrylate)s and compass motion model for internal motion of the fluoroalkyl side chain, *Macromolecules*, **32**, 1651-1660

[59] **Petit, F., Ilipoulos, I., Audebert, R. and Szőnyi, S.,** 1997. Associating polyelectrodes with perfluoroalkyl side chains: aggregation in aqueous solution, association with surfactants, and comparion with hydrogenated analogues, *Langmuir*, **13**, 4229-4233

[60] **Krupers, M.J. and Möller, M**., 1997. Semifluorinated diblock copolymers. Synthesis, characterization and amphiphilic properties, *Macromol. Chem. Phys*., **198**, 2163-2173

[61] **Galia, A., Pierro, P. and Filardo, G**., 2004. Dispersion polymerization of methyl methacrylate in supercritical carbondioxide stabilized with poly(ethylene glycol)-b-perfluoroalkyl compounds,*J. of Supercritical Fluids*, **32**, 255–263

[62] **Ma, Z. and Lacroix-Desmazes, P.,** 2004. Synthesis of Hydrophilic/CO2-Philic Poly(ethylene oxide)-b-Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) Block Copolymers via Controlled/Living Radical Polymerizations and Their Properties in Liquid and Supercritical CO2 *Journal of Polymer Science: Part A: Polymer Chemistry*, **42**, 2405–2415

[63] **Wells, S.L. and DeSimone, J.,** 2001. CO2 Technology Platform: An Important Tool for Environmental Problem Solving , *Angew. Chem. Int. Ed*., **40**, 518-527

[64] **Deniz, S., Baran, N., Akgün, M., Uzun, N. and Dinçer, S.,** 2005 Dispersion polymerization of methyl methacrylate in supercritical carbon dioxide using a silicone-containing fluoroacrylate stabilizer, *Society of Chemical Industry. Polym Int* **959**–8103

[65] **Bilgin, N., Baysal, C. and Menceloglu, Y. Z.,** 2005. Synthesis of Fluorinated Oligomers for Supercritical Carbon Dioxide Applications, *Journal of Polymer Science: Part A: PolymerChemistry*, 43, 5312–5322

[66] **Mai, Z. and Lacroix-Desmazes, P.,** 2004. Dispersion polymerization of hydroxyethyl methacrylate stabilized by a hydrophilic/CO_2-philic poly(ethyleneoxide)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (PEO-b-PFDA) diblock copolymer in supercritical carbon dioxide *Polymer*, **45**, 6789–6797

[67] **Woods, H.M., Nouvel, C., Licence, P., Irvine, D.J. and Howdle, S.M**., 2005. Dispersion polymerization of methyl methacrylate in supercritical carbon dioxide: An investigation into stabilizer anchor group, *Macromolecules*, **38**, 3271-3282

[68] **Erdik, E.,** 1998. Organik Kimyada Spektroskopik Yöntemler, Gazi Kitabevi

[69] **Erbil, H.Y.,** 2006. Surface Chemistry of Solid and Liquid Interfaces, Blackwell Publishing

[70] **Viitala, T.,** 2005. KSV CAM 200 Operating Manuel, rev.1.2, www.ksvltd.com

APPENDIX

Table A.1 Solvents and Non-solvents for Fluorine Containing Polymers

Polymer Name	Solvents	Non-solvents
HP-4 (PFDMA)	THF, Acetone, $CHCl_3$,Cyclohexanone	Bromobenzene, DMF, DMSO, TCE
HP-5 (PHFMA)	THF, Acetone, DMF, Cyclohexanone, Diethyl ether,	CCl_4, $CHCl_3$, Propylenecarbonate, DMSO,TCE
HP-6 (PTFMA)	THF, Acetone, DMF, Cyclohexanone,$CHCl_3$, DMSO	TCE, Bromobenzene, Toluene
BCP-1 P*t*BA-*b*-PFDMA	THF, Toluene, $CHCl_3$, Bromobenzene	DMSO, Propylenecarbonate
BCP-2 P*t*BA-*b*-PHFMA	THF, $CHCl_3$, Cyclohexanone, Diethyl ether,	Propylenecarbonate
BCP-4 P*t*BA-*b*-PTFMA	THF, Toluene, $CHCl_3$, Bromobenzene	DMSO, Propylenecarbonate
PP-1 P*t*BA	THF, Acetone, $CHCl_3$,Toluene, Diethylether, Cyclohexanone,	Water, DMSO,

AUTOBIOGRAPHY

She was born in 1981 in Istanbul. She had graduated from Erenköy Girl High School and attended to the Chemistry Department of Kocaeli University in 1999. The last year of academy in 2003, she had started to work in TUBİTAK-UEKAE as a researcher. In 2004, she was accepted as a master student to Istanbul Technical University, Polymer Science and Technology program in the Institute of Science and Technology. In 2006-2007 she started to work as a research assistant in TUBİTAK-NSF project in Gebze Institue of Technology. Her master thesis was supported both I.T.U and GYTE.